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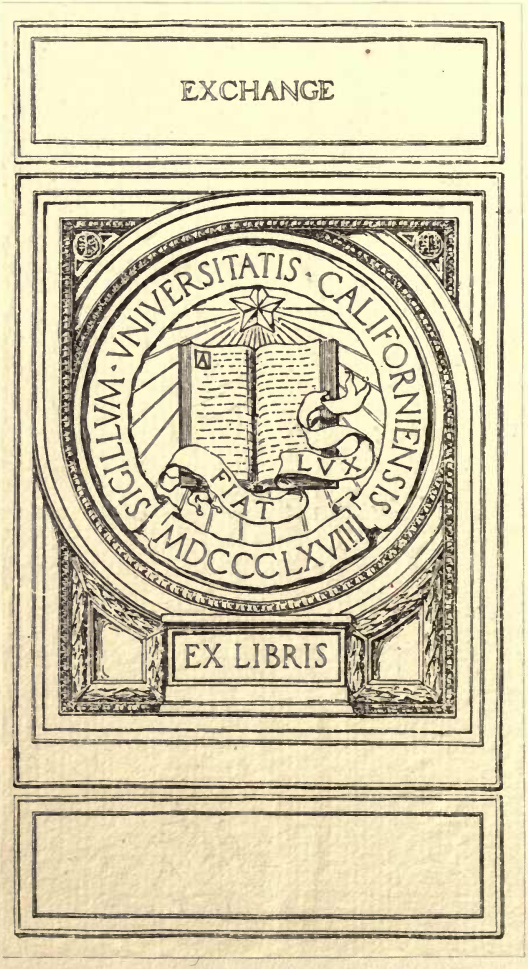

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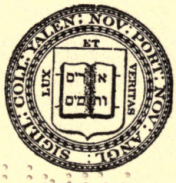

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TO

JACQUES LOEB

IN ADMIRATION OF HIS APPLICATION OF
PHYSICAL CHEMISTRY TO BIOLOGY

240954

THE SILLIMAN FOUNDATION

In the year 1883 a legacy of eighty thousand dollars was left to the President and Fellows of Yale College in the city of New Haven, to be held in trust, as a gift from her children, in memory of their beloved and honored mother Mrs. Hepsa Ely Silliman.

On this foundation Yale College was requested and directed to establish an annual course of lectures designed to illustrate the presence and providence, the wisdom and goodness of God, as manifested in the natural and moral world. These were to be designated as the Mrs. Hepsa Ely Silliman Memorial Lectures. It was the belief of the testator that any orderly presentation of the facts of nature or history contributed to the end of this foundation more effectively than any attempt to emphasize the elements of doctrine or of creed; and he therefore provided that lectures on dogmatic or polemical theology should be excluded from the scope of this foundation, and that the subjects should be selected rather from the domains of natural science and history, giving special prominence to astronomy, chemistry, geology, and anatomy.

It was further directed that each annual course should be made the basis of a volume to form part of a series constituting a memorial to Mrs. Silliman. The memorial fund came into the possession of the Corporation of Yale University in the year 1902; and the present volume constitutes the eighth of the series of memorial lectures.

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INTRODUCTION.

It is an exquisite honor to speak from this platform in this celebrated university where Willard Gibbs enunciated his standard work on "the theory of heterogeneous equilibria." I also feel very much indebted for the invitation to give a series of Silliman lectures, which have been delivered by the most prominent men of the scientific world. I therefore extend to you my warmest thanks for having conferred this rare distinction upon me.

The object of my lectures will be some chapters of modern physical chemistry. This branch of science has been treated in a rather great number of good or even excellent text-books, here as well as in Europe. It is therefore a difficult task to give something new and something which has not already before been worked out in a masterly manner. But it seems to me as imprudent as to carry owls to Athens to give you a course of physical chemistry as it is presented in the text-books. Therefore I have confined myself to some problems which are now under debate and which are still not finished but which promise the greatest interest for further investigations. Also when I refer to older investigations, I try to exhibit such facts as have not in a higher degree attracted the attention of the authors of text-books in this branch, and thereby to give a broader and more complete view of the exceptionally fertile field which we cultivate. I have often

found it useful to drag old historical data into the light especially in order to give an idea of the strict harmonical development of this subject, a circumstance which is often forgotten even to such a degree that physical chemistry is generally represented as if it had like Minerva sprung out quite fully developed from Jupiter's head.

What I wish to express to you is therefore something which according to my opinion supplements the excellent text-books which you already have perused. It is of course agreeable to me to lay before you my personal individual ideas. On the other hand it is quite clear that it would be a great mistake if my attempt were understood to be designed to embrace all the branches or even the most important branches of modern physical chemistry. But I feel quite sure that such an intelligent auditory as that to which I have the honor of speaking here will not commit this mistake and I trust the lacunæ of my exposition will be easily filled up by you who have been introduced so thoroughly into the different chapters of physical chemistry by your excellent scientific leaders and by the unrivalled interest which the enlightened scientific opinion here in America even more than in the old world attaches to this wonderful branch which is called physical chemistry and which is of the greatest use not only for the most important doctrines of the natural sciences and medicine but also for its far-reaching applications to modern industry. There are very few doctrines in exact science where so few lecture experiments are shown as in physical chemistry. This depends upon its theoretical character. The methods of working are

taken from the science of physics. There is almost only one chapter, which is so to say specially adapted for lecture experiments in physical chemistry, namely, that regarding catalytic action. For this chapter, a number of demonstrative experiments are worked out by Professor A. A. Noyes and G. V. Sammet in Boston. Another number of good lecture experiments are described in a little book by Professor Emil Baur in Braunschweig. It may suffice to draw attention to these expositions of the relatively small prominence of the experimental part of our science. The great progress in physical chemistry depends upon the quantitative measurements on which the general laws are based. In most cases it has been necessary to collect the evidence from a very vast field and an extraordinarily great number of experiments in order to get a view of the real situation of the problems and of the possibility of solving them. Chemistry works with an enormous number of substances, but cares only for some few of their properties; it is an extensive science. Physics on the other hand works with rather few substances, such as mercury, water, alcohol, glass, air, but analyses the experimental results very thoroughly; it is an intensive science. Physical chemistry is the child of these two sciences; it has inherited the extensive character from chemistry. Upon this depends its all-embracing feature, which has attracted so great admiration. But on the other hand it has its profound quantitative character from the science of physics. From this circumstance the great solidity and strength of our science is derived. The results of these quantitative measurements regarding the properties of a very great number of

substances is very difficult to present by lecture experiments; they must be given in diagrams and tables. I feel it necessary to explain from the very beginning why I have preferred to give a series of theoretical lectures rather than of experimental ones; the cause lies in the very character of the modern development of our science. Therefore modern physical chemistry is often called general or theoretical chemistry as in the two excellent German text-books of Ostwald and Nernst.

The theoretical side of physical chemistry is and will probably remain the dominant one; it is by this peculiarity that it has exerted such a great influence upon the neighboring sciences, pure and applied, and on this ground physical chemistry may be regarded as an excellent school of exact reasoning for all students of natural sciences.

UNIV. OF CALIFORNIA

LECTURE I.

SHORT HISTORY OF THE THEORY OF SOLUTIONS.

If we go very far back into antiquity we find how our modern chemical ideas slowly crystallised out from limited experiences and a naïve attempt at generalization. It is very interesting to find how solutions, which are now the chief material agent of the chemist, even at that time attracted the main attention. In a great number of the cosmogonic myths the world is said to have developed from a great water, which was the prime matter. In many cases, as for instance in an Indian myth, this prime matter is indicated as a solution, out of which the solid earth crystallized out.

Later on we find that Thales (624–523 B.C.) describes water as the origin of everything. Probably Thales had taken up this doctrine from ancient Egypt, which is according to all probability the country where the first very modest development of our science took place. Certainly the idea of the four primary elements, which is generally attributed to its prominent advocate the Greek philosopher, Empedocles (500 B.C.), is also of Egyptian origin. There are philosophers who regard one of the elements as the chief one, for instance Thales water, Anaximenes air, Heraclitus fire and Xenophanes earth, but water is generally preferred. Empedocles taught the doctrine of the transmutability of the four elements, that they were in a certain sense equivalent.

The doctrine of Empedocles was taken up by the

philosophers Plato and Aristotle whose ideas dominated the methods of reasoning until two hundred years ago and who still exert a great influence in the philosophical sciences. In Plato's work Timaios we read: "We believe from observation that water becomes stone and earth by condensation, and wind and air by subdivision; ignited air becomes fire, but this when condensed and extinguished, again takes the form of air, and the latter is then transformed to mist, which coalesces into water. Lastly rocks and earth are produced from water." Evidently the four elements of antiquity correspond nearly with what we now call states of aggregation. The ancients had observed the transformation of water into steam and vice versa, this phenomenon as well as the deposition of solid substances from solutions or suspensions in water was the chief one upon which they built their theory. Under all circumstances water was the chief material from which they gained their experience.

In antiquity the chief products of industrial chemistry were the metals. Plato and especially Aristotle developed the idea of transmutation of the metals. Even in this department the condition of fluidity seemed to be most valuable for the reactions and therefore the fluid metal, mercury, attracted the attention of the chemists more than the other metals did. It tinged the metals generally silver-white and was supposed to be the prime matter of all metals. This prime matter was called the "mercury of the philosophers" and regarded as the "ghost" of the metals, which was the bearer of the metallic properties. In Egypt lead seems to have played a similar role and therefore received the name

of "Osiris" from the principal deity of the old Egyptians. A rather moderate heat is sufficient for converting lead into the liquid state, in which it acts as a solvent on other metals. Olympiodoros says "Osiris is the principle of everything liquid, it is Osiris, which causes the condensation in the sphere of fire." Under the name of lead or "Osiris" also tin "the white lead" in contradistinction to the common or "black lead" was included. In many minerals from which lead was extracted a small quantity of silver is contained. This could easily be separated from the lead and as the silver was more valuable it was regarded as "the perfect lead." These considerations are quite characteristic of the reasoning of the alchemists. When mercury was discovered, about the time of the Peloponnesian war, it was found much more satisfactory for dissolving and tinging metals than lead and was therefore supposed to be the "materia prima." The readiness with which it could by evaporation be separated from other metals made the experiments with mercury much easier than those with lead.

The liquid state was already at that time found to be the most suitable condition for chemical reactions. The chemistry of the Middle Ages up to the seventeenth century retained the same view. In the writings of Isaac Hollandus (at the beginning of the 15th century) we read that "the philosophers have followed the direction given by Nature and at first transformed everything to water" (i. e., dissolved it) "before they used it in the art of chemistry." According to van Helmont (1577–1644), the greatest chemist of his time, and the discoverer of carbonic acid (gas sylvestre),

"water is the primary element, into which all substances may be reduced." Boyle, the father of modern chemistry (1626–1691) opposed the ideas of Aristotle and his alchemical successors regarding the four elements; he expressed the opinion that only such substances should be called elements, which are undecomposable constituents of matter, but in his "Sceptical chymist" he still expresses the opinion that water may be transmuted into all other elements."

The experience of the alchemists was summed up under the formula "the Substances do not act upon each other unless they are dissolved" (corpora non agunt nisi soluta) or that the salts do not give any reaction, if not dissolved, and then not too much diluted (Salia non agunt nisi dissoluta, nec agunt si dissoluta nimis). This last part of the sentence evidently refers to the circumstance that precipitations, which are often observed after mixing solutions of two different salts, do not occur, if the solutions are too dilute, so that the liquid retains the newly formed salts in unsaturated solution. Van't Hoff and Le Chatelier find also that reactions proceed much more regularly, when the reacting substances are dissolved, than if they are not.

As the solubility of a substance was regarded as the necessary condition for its entering into chemical reactions, the great problem of chemistry was to find a solvent for all possible substances. This hypothetical solvent was called "alcahest" by Paracelsus (1493–1541). The alcahest was regarded as "the stone of the wise" or as the "life-elixir" and very many receipts for its preparation were given. Kunckel (1716) gives a very satirical and severe criticism of these receipts,

when he says that the great problem was to find a vessel which would not be dissolved by the alcahestic liquid, otherwise there would be no possibility of using it.

The most celebrated natural philosopher of antiquity was Democritus of Abdera (born 460 B.C.). He had proposed an atomic theory, according to which matter consists of discrete atoms with empty interstices. Plato taught that the molecules of one substance might enter into the interstices between the atoms of another substance. Aristotle opposed the atomic doctrine. Through his great authority the revivification of the atomic theory was hindered until Gassendi (1592–1655) took up and elaborated the ideas of Democritus. According to Gassendi a number of atoms could unite to form molecules. Solution depends then upon the particles of the substance, which goes into solution, entering into the pores of the solvent. As the particles of common salt were regarded as small cubes according to the crystal form of this substance, it was said that this salt filled up the pores of cubical form between the water-particles. If all the cubical pores were so filled up, the salt-solution was saturated and could not dissolve more salt. It was known that other salts, *e. g.*, the octahedral alum, might be taken up by the said solution. Therefore it was supposed that the water contains other pores of octahedral form, into which the alum but not the common salt could enter.

This so-called corpuscular theory was used by Boyle in his investigations and won through this circumstance a great credence. It was propagated in the highest degree by Lémery's "Cours de Chimie," the most-used

text-book on chemistry at that time (first ed. 1675, last 1756). In order to explain the capacity of acids to act as solvents for metals it was supposed that the particles of the acid were very sharp and pointed, so that they entered easily between the particles of the metals and tore them from each other by their violent motion. This acute angulated form of the acid particles was also evident from the shape of their crystals, which was described as acicular, as well as from their sharp taste. The alkalis were supposed to possess pores in which the points of the acid particles were broken off, so that the acid lost its solvent properties and a salt resulted. Réaumur explained in a similar manner the fact that a contraction takes place if alcohol is dissolved in water. It was also supposed by Réaumur that water could fill up the pores between the particles of crystals, *e. g.*, of sulphuric acid; this is the first time that the idea of water of crystallization is mentioned.

It is clear that this theory of solution could not be satisfactory. It was necessary to suppose all possible kinds of interstices in the different solvents and the widely varying solvent power of different solvents found no explanation. At that time Newton's great discoveries were evoking the admiration of the scientific world. Newton himself supposed that the universal force, acting between the celestial bodies, was also able to bind together two different substances and cause their union to a new system. He maintained that a salt is dissolved by water if its particles exert a greater attraction on water-molecules, than on each other. This doctrine was accepted by the founder of the phlogiston-theory, Stahl, and in general by the scientific world and is in

a certain sense prevalent at the present time, although we do not suppose that the chemical forces are of the same nature as that of gravitation. Very interesting is another statement by Newton namely that the dissolved molecules tend to get away from each other as if they were gifted with a repulsive force against each other. This view reminds one very much of the modern theory of osmotic pressure which is regarded as analogous to the pressure of a gas. So-called affinity-tables were now constructed in which was tabulated the extent to which a certain substance is soluble in a given solvent. But even at an early stage it was found difficult to maintain the parallel between affinity and gravitation. This latter force is independent of the other properties of the attracting substances and determined only by their mass, whereas the solubility is in the highest degree dependent on the kind of matter contained in the solvent and solute. Buffon therefore added to the Newtonian hypothesis a secondary one, according to which the form of the molecules was of very great importance in the phenomenon of solution, where the molecules come into the very closest contact with each other, whereas in the case of gravitation the molecules of the two acting bodies lie at such great distances from each other that their form is of no importance.

This idea was accepted with great approval by the leading chemists. It was found as a general rule that a certain similarity prevails between two substances which mix with each other in a solution (similia similibus solvuntur), and this rule has retained its value until the present day.

It was also evident that the solution of a salt or of cane sugar in water is a process of a very mild kind, for it is possible to separate the solvent from the dissolved body by simple distillation. The solution of a metal in an acid on the other hand gives a chemical change of a much more deeply seated nature, a salt is formed, which differs totally from both the metal and the salt, and it is generally very difficult to recover either the metal or the acid from the salt. Lavoisier therefore called this latter process dissolution in contradistinction to simple solution. Upon dissolution a real chemical decomposition of the solvent and the solute takes place. On the other hand the process of solution consists according to Lavoisier simply in a separation of the molecules of the dissolved substance, which suffers no real chemical change.

Lavoisier directed attention to another circumstance. He reasoned in the following manner. If I heat a salt to a sufficiently high temperature it becomes liquefied, just as by the use of a solvent. It seems obvious from this circumstance, that if heat and a solvent are applied simultaneously to the salt their concurrent action will be greater than that of either alone. In other words the solubility should increase with temperature. This corresponds very well with the facts of every-day experience, and was a familiar fact to the alchemists. For Lavoisier the conclusion seemed still more evident as heat at that time was regarded as a form of matter ("caloric") analogous to the solvent water, although of a finer kind. It was not known by him that some substances diminish in solubility with increasing temperature. Even liquefaction is not perfectly analogous

to solution, otherwise one would expect that two liquids would mix in any proportions, which is certainly the case with many pairs of liquids such as alcohol and water, but is not so with many others, for instance oil and water, a fact which was very well known from the earliest times.

The ideas of Lavoisier were not accepted by the majority of the alchemists at that time. Richter (1793) is of the opinion that a certain affinity causes solution. Thus for instance he says that it is possible to precipitate salts from their solutions in water by adding some substance, such as alcohol, which has a greater affinity for water than the salt has. In the same manner, he says, a deliquescent salt takes up water from the air and gives a solution, "because the salt has a greater affinity for water, than the air has." These examples especially the latter one, indicate that his views do not stand very severe criticism.

The same is the case with the renowned physico-chemist Berthollet. He was of the opinion that the components of chemical compounds do not enter into them in constant proportions and that solutions are typical chemical compounds of variable proportions. He observed that if mercury-sulphate is dissolved in water real chemical changes take place and he believed that these changes do not occur according to constant proportions. There is in his opinion only a difference of degree between a solution and a very well defined chemical compound. Hence he was induced to deny the law of constant proportions in chemical compounds. It is well known that he was defeated in the battle with Proust on this point. Proust conceded that water

might enter into combination with certain substances, e. g., salts. These compounds are known in the crystalline state under the name of crystal hydrates. They, as well as other chemical compounds, are characterized by their constant composition. (Later on it has been found by Mallard and Klein that the zeoliths may lose a part of their crystal water without changing their form of crystallisation; other examples of similar kind are given by Tammann and by Loewenstein).

Berthollet argued that not only the solution of solid or liquid substances in liquids but even the solution of gases in liquids is due to a chemical process. In this latter case the dissolved quantity of the gas is dependent on the pressure of the gas and for weak solutions simply proportional to that pressure. Of course it is possible to suppose that in this case an attraction takes place between the dissolved gas-molecules and the solvent. But if as for instance with oxygen, hydrogen or nitrogen in water the concentration of the gas-molecules is less in the solution than in the gas above (which also contains some molecules of gaseous water), it will be necessary to suppose that the attraction of the gas-molecules to the fluid water is less than that to the sparingly distributed water-molecules in the gas-phase, an absolutely untenable idea.

From this time dates the still actual discussion whether solution is a physical or chemical process. Even at that time it was considered that the contraction or the heat effect usually observed when a substance is dissolved or its solution diluted, is a certain indication of a chemical process. On the same ground it would be right to suppose that similar phenomena observed at

the freezing of a liquid indicate that freezing is a chemical process. Berthollet seems also to have held this opinion. But the majority of scientists regard solidification as a physical process. On the other hand it must be conceded that this process is of absolutely the same nature as the conversion of one allotropic modification of a substance into another, for instance monoclinic sulphur into rhombic sulphur. In reality there is no sharp limit between physical and chemical processes. The best definition to decide between a physical and a chemical process is the following: In a physical process the molecules of the acting substances undergo no change, in a chemical process a change of the molecular structure occurs. In many cases the change is extremely insignificant and then the decision is difficult. For instance the abnormal behaviour of water, in showing a maximum of density at about 4° C. is certainly due to the presence in the water of two kinds of water-molecules, the water-molecules proper and the ice-molecules, which are in chemical equilibrium. With lowering of the temperature this equilibrium is changed, some of the water-molecules proper are transformed into ice-molecules. Thereby the volume increases just as when water freezes to ice. Of course the ice-molecule has another structure (probably more complex) from that of the water-molecule. It would therefore be right to say that on cooling water below 4° C. a chemical process takes place. But the properties of the water change so very little in this process that most people agree to call it a physical process. In reality it is a combination of a physical and a chemical process. The ice-molecules as well as by far

the greater number of the water-molecules remain unchanged when the temperature is lowered between + 4° C. and 0°. These molecules are therefore only subject to physical processes. Probably a very small number of the water-molecules undergo a change of structure so that they are transformed into ice-molecules. These molecules are obviously subject to a real chemical change. But this process is rather unimportant and is therefore mostly neglected.

In the same manner if we have acetic acid, say in 1 per cent. solution, the dissociation theory says that about one per cent. of the CH_3COOH molecules are (at 25° C.) decomposed into their ions CH_3COO and H. If we dilute this solution to double its volume with water, the number of the dissociated molecules increases in the proportion 1.41 to 1 at the expense of the undissociated molecules. The 98.6 per cent. of undissociated molecules remain unchanged, only 0.4 per cent. of them being split up into their ions on dilution. In this case the chief process is certainly only a physical one, and most scientists therefore agree in regarding the whole process as a physical one although 0.4 per cent. of the acetic acid molecules undergo a rather important change of structure. Perhaps in this case also a very slight hydration takes place, which must be regarded as a chemical change—an addition of water to the acetic acid molecule, but such a process is about of the same degree of insignificance as the transformation of water-molecules to ice-molecules. It is therefore no wonder that it is regarded as a physical one, although some very slight chemical change occurs at the same time. On the other hand the transformation of water

into ice is probably mainly a chemical process, because in the water at 0° C. the overwhelming proportion of the molecules is of the water-molecule kind and only very few ice-molecules occur. All those are at the congelation transformed into ice-molecules, a chemical process. Therefore the freezing of water should properly be regarded as in the main a chemical process. Most scientists say that it is a physical one. Such an assertion is connected with the ease with which it is carried out in the direction from water to ice, as well as in the opposite direction from ice to water. If we do not take the very unstable super-cooled water into consideration, the two modifications of water, namely fluid water and ice do not exist both together at any temperature except 0° C. (at ordinary pressure), and if an ice-crystal is brought into contact with the supercooled water the latter very rapidly freezes to ice with an elevation of the temperature to 0° C. On the other hand the transformation of rhombic sulphur into monoclinic or inversely takes place very slowly even in the presence of the modification stable at the temperature under consideration. Still more is this the case with common and grey tin. The latter is stable below 18°, as Cohen has shown, but is very rarely found. On common tin which has been inoculated with it, it grows slowly at the expense of the former at temperatures below 18°. Evidently the great velocity of reaction in the case of water depends upon the presence of a fluid phase, the water. Superheated ice is not known, whereas the two allotropic modifications of sulphur or of tin are very well known to exist as well below as above the so-called point of transition.

These processes which only are reverted with relative difficulty, are by preference regarded as chemical processes.

Quite recently, after the evolution of the theory of electrolytic dissociation the doctrine of the utility of solvents for the progress of chemical reactions has been put in a new light. This is especially true for water, but also for alcohols and many other solvents, in which dissolved substances dissociate into their ions. Gore had for instance observed that the ability of hydrochloric acid to dissolve oxides and carbonates of the alkali-metals or alkaline earth-metals depends upon the presence of water. This was stated by Hittorf, who did not believe that Gore's experiments were conclusive, and even he found the same peculiarity with anhydrous hydrobromic and hydriodic acid. The water-free acids are non-conductors of electricity and do therefore not contain ions in appreciable degree.

Most reactions and especially the most important ones in inorganic chemistry are due to ions—they are characterized by their instantaneous accomplishment. This idea is carried out by Ostwald in his treatise on chemical analysis.

The presence of moisture is of the greatest importance for many reactions, as has been shown by Dixon and Baker. This action of water is often attributed to the formation of small, generally invisible droplets, in which the reacting substances dissolve. This view has been emphasised by D. K. Zavrieff.

It would be too rash to conclude from these observations that other substances than (the common) ions do not react. The formation of nitro-compounds of

derivatives of benzol, for instance, is not due to the ions H or NO_3 of nitric acid. The reaction goes on the more rapidly and the reaction is the more complete, the higher the concentration is of the nitric acid. For producing the tri-nitro-derivates an addition of oil of vitriol is necessary, which binds the water formed during the process (for instance in the nitration of benzene):

$$C_6H_6 + HONO_2 = H_2O + C_6H_5 - NO_2$$

Probably benzene is to a very small degree dissociated electrolytically into the ions H and C_6H_5 and the nitric acid in high concentration into NO_2 and OH of which H and NO_2 are positively charged. On addition of water the ions HO and NO_2 decrease and are transformed into the ions H and NO_3. Therefore the reaction diminishes. Of course this view is only a modern modification of the old conception of radicals. Similar ideas may be adapted for the explanation of any chemical reaction from the electrolytic standpoint.

Sometimes it has been stated that water is not favorable for reactions. Thus H. Goldschmidt and his pupils found that the formation of esters of organic acids with alcohol is hampered by traces of water. Goldschmidt expressed the opinion that the hydrogen ion of the acid forms a complex ion $C_2H_5OH.H$ through addition of alcohol. This ion, he supposes, is the really reacting one and is spoiled by the presence of water. (It seems to me more simple to suppose that alcohol is partially dissociated into the ions C_2H_5 and OH and that the C_2H_5 ion decreases on addition of H.OH with its relatively great quantity of OH-ions, and that the ion C_2H_5 replaces the H ion in the acid). Similar circum-

stances have been observed in a great number of reactions in organic chemistry. Here is a vast field of interesting investigations for the extension of the theory of electrolytic dissociation.

LECTURE II.

THE MODERN MOLECULAR THEORY.

At the end of the eighteenth century a great development of chemistry took place and from this time we date modern chemistry. It is usually said that we are indebted to Lavoisier for this wonderful progress. I believe it is better to say that the great change was due to the application of quantitative methods in chemistry. Certainly there had been quantitative measurements made before but only on a small scale. It was at that time that Cavendish made his excellent measurements, amongst which the determination of the composition of water was the for our science most significant. Lavoisier seems to have known of this experiment, but he made it anew and carried out some new analogous experiments in which he proved that the quantity of matter is not changed in chemical reactions, a view which had already been expressed by van Helmont (1577–1644). But it was Lavoisier who with admirable consistency carried through this idea and so inaugurated a new era. Yet he was not alone, the time was ripe for the revolution of chemical science. Richter studied (1792–1794) the phenomenon of neutralization of solutions and found that if a certain quantity of an acid solution neutralizes a given quantity of alkali and the same is true for a definite quantity of another acid solution, then these two acid solutions are also equivalent in the neutralization of a

second basic substance. Further Scheele had found that some metals can attain to more than one stage of oxidation. Richter came to the conclusion that these different stages neutralize quantities of one and the same acid, which are proportional to their content of oxygen. In his controversy with Berthollet Proust proved that there may be different stages of oxidation of the same substance, e. g., iron and tin, but that no intermediate products between the few well-defined compounds of constant proportions are to be found. It is very remarkable, that, as Le Chatelier says, Proust's analyses, from which he deduced his conclusions "were often very poor, and he gave analyses, which did not at all correspond with the facts."

Quite the same we may say of Dalton. In his first publication (1803) he gave the following analyses, in which N expresses 4 unit-weights of nitrogen, O 5.66 of oxygen, H 1 of hydrogen, C 4.5 of carbon and S 17 unit-weights of sulphur:

Nitrous oxide ... N_2O	Ammonia ..... NH
Nitrous gas ..... NO	Oxide of carbon .... CO
Nitrous acid .... N_2O_3	Carbonic acid ..... CO_2
Nitric acid ..... NO_2	Sulphurous acid .... SO
Water ..... HO	Sulphuric acid ..... SO_2
Marsh gas ..... CH_2	Olefiant gas ..... CH.

According to these figures the anhydride of sulphuric acid ought to contain double the quantity of oxygen for the same weight of sulphur as sulphurous acid whereas we now know that this ratio is as 3:2. Water has according to Dalton the composition 1 part of hydrogen to 5.66 oxygen, the right proportion is 1 to 8, and so forth.

It is said that Dalton was the founder of the modern

atomic theory and although that is to a certain extent true, yet on the other hand it is just as certain that, if Dalton and Proust had not very firmly believed the atomic theory, which prevailed at that time, they would not have been led to its foundation through their very imperfect analyses. Yet there was something new of great importance in their atomic theory, compared with that of the old Greek philosophers. The latter had only said that matter was built up of atoms of different size and form. They did not recognize what we call elements, their elements corresponded to qualities. Therefore they had no ground to suppose that the atoms of the same substance have always the same mass. But the hypothesis that this is the case is most obvious as Dalton explains. Water, he says, has always the same composition. If then it always contains the same number of hydrogen and of oxygen atoms, as he believed, the only reasonable explanation is to suppose that all atoms of hydrogen are absolutely similar to each other, and that a given atom of oxygen does not differ at all from any other atom of oxygen.

Immediately after these experiments Wollaston showed that Dalton's law of multiple proportions is also valid for the neutralization of acids with bases. So, for instance, he gave an analysis indicating that bicarbonate of sodium contains double the quantity of carbonic acid to the same weight of sodium, as the monocarbonate does. At the same time that Dalton was working Berzelius was executing with marvellous diligence a great number of excellent analyses of the most varied substances, and all chemists followed his example and carried out accurate quantitative measurements.

In 1805 Gay-Lussac discovered the fundamental law that the volumes of two gases, which combine to form a compound, stand in a simple numerical relation, for instance the volumes of hydrogen and oxygen entering into water are in the proportion 2 to 1, those of hydrogen and nitrogen entering into ammonia as 3 to 1, etc. This discovery led later on to the law of Avogadro.

From the beginning of the last century the system of quantitative measurements had put its stamp on chemistry and from that time dates modern chemical science rather than from the time when oxygen was discovered. The great progress made in chemistry towards the end of the last century when modern physical chemistry was inaugurated, depended also upon the introduction on a large scale of new quantitative measurements.

After Dalton had established the law of multiple porportions it would seem that the atomic theory had won an absolutely undisputable victory for all times. When the mechanical theory of heat had begun its triumphal march through the exact sciences it allied itself with the atomic theory as an equal, the kinetic theory of gases was born and developed by the foremost physicists, such as Clausius, Maxwell, and Boltzmann. They calculated the motions and magnitude of the atoms and their compounds, the molecules, with nearly the same certainty as an astromoner calculates the magnitudes and the motions of the components of double stars. The atomic theory was regarded as the firm foundation of the exact sciences.

Then at the end of the last century came the reac-

tion. A Bohemian chemist, Wald, argued in the following manner. It is true that chemical compounds have a constant composition, but only because we demand that they shall have it. The manufacturer subjects them to different physical and chemical processes such as recrystallization, repeated distillation, conversion into new compounds and back again until the composition is not changed by them but the same product, that is, a product with constant physical and chemical properties is obtained again and again. These different properties are of course dependent upon the composition of the product, in other words the manufacturer of chemical products takes good care that these products shall have a constant composition. And according to Wald, Nature proceeds in the same manner. But this does not help to explain why we always find the same ratio between the weight of, *e. g.*, oxygen and hydrogen in all the innumerable organic compounds which we now know, or else a simple multiple of this ratio. To explain this fact a new law must be introduced, which expresses just this assertion or is equivalent to it. Ostwald has given this law the name of "the law of integral reactions."

There is still a difficulty with this new conception. There exist in nature substances of the same composition but of different properties. The simplest case is that of oxygen and ozone. The law of Avogadro leads to the conclusion that if a molecule of oxygen contains two atoms then a molecule of ozone contains three atoms. The atomic theory gives a new mode of variation of properties, than that due to alteration of composition, namely that depending on change of

configuration in space. Nature also gives instances of this higher degree of variability. The opponents of the atomic theory ought therefore to invent some other explanation than that of Wald, otherwise their case remains rather weak.

Nevertheless Wald's ideas found a number of adherents, some of them possessing the highest authority such as Le Chatelier and Ostwald, and the latter has worked out a whole system of chemistry on the foundation laid by Wald. By far the greater majority of chemists had not listened to the new doctrines, when a wholly new aspect of the question came up. Eighty-four years ago (1827) an English botanist, Robert Brown, found with the aid of the microscope that small particles, *e. g.*, grains of pollen, suspended in a fluid, possess a zig-zag movement, which was the more considerable the smaller the particles considered were. This peculiar kind of motion was examined by a great number of scientists, from Regnauld 1857 to Gouy 1888, and they stated one after the other, that the motion in question increases with the smallness of the particles, the fluidity of the surrounding fluid and the temperature. It was, to put it briefly, analogous to the motion, which the adherents of the kinetic theory of gases attributed to the molecules of a gas. Consequently it was called the Brownian molecular movement. In recent times this interesting phenomenon has attracted very great attention. Einstein and v. Smoluchowski have developed the theory of it. Svedberg, Ehrenhaft and especially Perrin have investigated it experimentally. The simplest case is found in suspensions in air, studied by Ehrenhaft. He evaporated silver in an electric arc.

The vapours condensed to extremely small drops. According to Stokes' law these droplets would fall the more rapidly, the greater their magnitude. By these means Ehrenhaft could separate them from each other according to their size and when he knew the time required for their subsidence he could calculate their dimensions. Their diameter was in one experiment only about the thirty thousandth part of a millimeter, so that they could only with difficulty be observed with the aid of an ultramicroscope. He measured their movement and found it to be 0.046 millimeter per second, whereas a formula of v. Smoluchowski demanded 0.048 millimeter per second, a really good agreement.

Perrin has worked out his experiments on a very large scale. He used suspensions of gamboge or mastich in water. He determined the distance, d, between the position of a droplet at the beginning and at the end of a certain time (t). The droplet describes a straight line which is suddenly altered to a new direction every time that the droplet in its movement collides with a molecule. Einstein has deduced the following formula:

$$d^2 = t\frac{R.T}{N}\frac{1}{3\pi.a.b},$$

where R is the gas-constant of Avogadro's law, T the absolute temperature, a the diameter of the droplet, b the viscosity of the surrounding fluid and N the number of molecules in one gram-molecule. a was determined by means of Stokes' law from the velocity with which the droplets fell in water, b is known, as well as

R and π. T, t and the corresponding values of d were determined experimentally. He found $N = 68.10^{22}$.

Perrin determined the value of N in another way. The kinetic theory demands that the rotatory energy of a droplet should be of the same magnitude as its translatory energy. From this theorem Einstein deduced a formula connecting N with the velocity of rotation of a droplet. The droplets convenient for measurements of this kind must be relatively large; Perrin used one of 0.0115 millimeter diameter. Thanks to foreign matter, often appearing in such droplets, it is possible to determine their velocity of rotation. The droplets were maintained floating in a solution of urea of their own density. Perrin found the number $N = 65.10^{22}$.

Perrin invented yet a third method of determining N. It is well known that the density of our atmosphere decreases with increasing height. This depends upon the weight of the upper air-layers, which compress the lower ones. The rate of decrease of the density upwards is proportional to the weight of one molecule (according to the gas-theory). Now Perrin inquired whether the same phenomenon occurred in his emulsions—in this case the molecules are the droplets and their weight is diminished by the weight of an equal volume of water. He found his expectations fulfilled and could by the aid of the microscope count the number of droplets in different heights from the bottom of the vessel containing the suspension. From these observations he could calculate how many times one of the droplets was heavier than a molecule of, for instance, oxygen. Further, he could from the known

diameter of the droplets and the difference of their specific weight and that of the surrounding fluid calculate the weight of each droplet in the fluid. Hence he could calculate the absolute weight of a molecule of oxygen and as a grammolecule of oxygen is 32 grammes the number N of the molecules is 32 grammes of oxygen. He found a value of $N = 71.10^{22}$.

All the three values determined agree exceedingly well with each other and not less satisfactorily with the number of N, found by other methods. These are taken from different parts of physical science. Faraday's law demands that the total charge of the ions contained in 1 gram of hydrogen or an equivalent quantity of any other substance, which occurs in the form of electrolytic ions, should be 96,550 coulombs. Now Rutherford, Geiger and Regener have counted the number of α-particles which leave a given quantity of radium per second and they have also measured the quantity of electricity on a single α-particle, which is an atom of helium with a positive charge. Supposing now that an atom of helium is charged according to Faraday's law and equivalent to two atoms of hydrogen, Rutherford calculated $N = 62.10^{22}$. Dewar directly measured the quantity of helium developed during a certain time from one gram of radium and found from Rutherford's figures of the number of helium-atoms thrown out by a gram of radium per second, that $N = 71.10^{22}$. Boltwood calculated the quantity of α-particles emitted by one gram of radium and the corresponding number of radium-atoms decomposed in a certain time and compared this quantity with the observed rate of decomposition of radium. From this calculation the result is obtained that $N = 71.10^{22}$.

Another method of calculating N from the constants of heat-radiation gave according to a theory of Lorentz $N = 71.10^{22}$, according to a theory of Planck $N = 62.10^{22}$. Townsend determined the charge of droplets condensed from steam by means of Röntgen rays. He and his successors found, if they applied the law of Faraday, $N = 62.10^{22}$ (on the average).

There are several other methods of less accuracy but which give the same order of magnitude. Thus Cauchy determined (1835) the number of molecules, which when laid behind one another at molecular distance on a straight line would give the wave length of the yellow light of sodium to be about 600. Similar determinations in modern times are due to Erfle, and although the different gases do not give the same values as one might expect (the variation is about as 3 to 4), they agree well on the average with the figures of Perrin. Lord Rayleigh determined the number N of molecules in a grammolecule from the diffusion of light from the sky and found N about 70.10^{22}. Also from the internal friction of gases when compared with the volume in the condensed state or the refractive index, the dimensions and number of the molecules has been deduced, giving N about 45.10^{22}.

When we know the number N it is easy to calculate the diameter of the molecules. It varies between about 2.10^{-8} and 6.10^{-8} cm.

We see then that the molecular or atomic theory has attained a very high degree of probability through these recently made measurements. Ostwald has openly conceded that this theory does not seem open to question but that one must admit a granular structure of matter.

But not only matter is regarded as having an atomic structure. In 1870 Helmholtz indicated that the most simple way of interpreting the law of Faraday is to suppose that there exist ultimate small quantities of electricity, which are all of the same magnitude and that one of these electrical particles, now called electrons, is what is united with a monovalent ion. It has not yet been found possible to isolate a positive electron, but the negative electrons occur in the so-called cathode-rays or β-rays. It is therefore now generally admitted that the charge of positive ions is due to the loss of negative electrons. The ultimately small quantity of electricity is about 46.10^{-10} electrostatic units and it was, as a matter of fact, the determination of this electrical quantity which led to the calculation of the number N by means of electrical methods and which yielded concordant results before the direct measurement of N by Perrin and Ehrenhaft on suspended particles.

Science changes its aspect very rapidly nowadays. When Ehrenhaft measured the movements of electrically charged particles under the influence of gravitation and electric forces, he observed that the electric forces and hence the electric charges found for different single particles were not of the same magnitude but differed from one another in a rather high degree. The old determinations of the atomic charge were all founded on a mean of the movements of the charged particles. Now Ehrenhaft studied the behaviour of a single particle. He prepared these particles by evaporating the noble metals gold, silver or platinum in the electric arc. These particles were as a rule very heavy

so that the Brownian movement did not render the observations difficult. In moist air or if temperature-currents were not excluded the Brownian movement was very perceptible. The same was the case with the droplets formed in the neighbourhood of a piece of yellow phosphorus.

The charge of the metallic particles observed by Ehrenhaft varied for platinum between 0.9 and 12.10^{-10} units (instead of the constant charge $4.65.10^{-10}$ units), for silver between 0.9 and $26.7.10^{-10}$ units and for gold between 0.5 and $9.6.10^{-10}$ units. It seemed therefore that charges about ten times less than the charge of an ion may sometimes occur. Amongst the observed charges some are found to possess a preponderating frequency and these commonly occurring charges do not differ very much from the mean electric charge observed by himself and his predecessors. Simultaneously with Ehrenhaft (1910) Millikan arrived at similar results.

The observations of Ehrenhaft were continued by K. Przibram. He investigated the charge of droplets formed during electrolytic production of oxygen or upon the admixture of air, through which electric sparks had passed, with moist air, or in the evaporation of hydrochloric acid in air ionized by means of Röntgen-rays or finally formed in the neighbourhood of yellow phosphorus in air. He arrived at results which agree very well with those of Ehrenhaft.

In Przibram's measurements the individual charges varied for electrolytic oxygen between $1.4.10^{-10}$ and 170.10^{-10} electrostatic units, for particles produced by electric discharges in moist air the corresponding figures

were 1.7 and 191, for drops in nebulae from hydrochloric acid 2.2 and 60, and finally for drops from nebulae in moist air in the presence of phosphorus in one series of about 180 measurements 0.7 and 120 in another series with about 1000 single measurements where we might have expected a greater variation, 2.7 and 52 respectively. It is very difficult to see a simple way out of the difficulties raised by Ehrenhaft and Przibram. A charge of 10^{-10} electrostatic units per particle corresponds to $1.29.10^{20}$ molecules in one cc. of gas at 0° and 760 mm. pressure or $28{,}900.10^{20}$ molecules in one grammolecule. If the charge of a single particle is $n.10^{-10}$ electrostatic units the number of molecules is n times less.

In his observations the frequency of different charges shows a periodicity with maxima in nearly equal distances. Thus the mean distance of the thirteen maxima in a series of observations with droplets from phosphorus is $4.7.10^{-10}$ electrostatic units, very near to the atomic charge according to older measurements. Yet even this regularity seems to be to a certain degree fortuitous. In series carried out on different days with droplets from phosphorus Przibram found this interval varying between 3.10^{-11} and 7.10^{-10} electrostatic units. The general mean was still $4.6.10^{-10}$ units. The cause of this peculiar variation is still undetected. In order to get a reliable average value it seems necessary to make thousands of single observations.

In some hundred cases Przibram succeeded in measuring the charge of the same droplet twice during its fall, and he found that in many cases a discharge had taken place.

It should be mentioned here that de Broglie has carried out similar measurements to those of Ehrenhaft without finding corresponding anomalies. A concise summary of the present state of the question of the atomistic structure of electricity is given in the table below, reproduced from Ehrenhaft's last memoir.

Table of the chief determinations of the unit charge, according to F. Ehrenhaft.

		e. 10^{10}	
R. v. Helmholtz and Richarz	1890	1.29	Quantity of electricity at electrolysis. Loschmidt's number of atoms in a cubic centimeter gas.
H. A. Lorentz and E. J. Stoney	1890	1.29–6.1	
T. S. Townsend	1898	1.2–1.5	Falling nebula of drops. Stokes formula. Determination of the total charge.
R. T. Lattey	(1909)	5	
J. J. Thomson	1898–99	6.5–6.8(6.0–8.4)	Falling nebula of drops. Stokes formula. Determination of the total charge.
M. Planck	1901	4.69	Constants of radiation entering in the formulae of Stefan and W. Wien (Planck).
I. Nabl	1902	2	Charges of gases with drops from Wehnelt-interruptor.
J. J. Thomson	1903	3.4 (3.3–3.5)	Ionization through radium.
H. A. Wilson	1903	3.1 (2.0–4.4)	Falling of water drops in electric fields.
H. Pellat	1907	2.46–6.9	Mobility of ions in electrolytic solutions.
K. Przibram	1907	3.8 (1.7–6.2)	Falling of alcohol drops in electric fields.
R. H. Millikan and L. Begeman	1908	4.03 (3.66–4.37)	Method of H. A. Wilson.
E. Rutherford and H. Geiger	1908	4.65 (4.15–5.5)	Counting of α-particles, measuring of charge.

E. Regener 1908	4.79	Counting of α-particles, measuring of charge.
R. Tabor and R. T. Lattey....1909	4.47 (3.13–5.74)	Electrolytic nebula of oxygen.
A. Alexejew and M. Malikow 1909	4.5 (3.0–6.3)	H. A. Wilson's method
F. Ehrenhaft.....1909	4.46–4.68	Single particles falling in air.
G. Moreau 1909	4.3 (4.1–4.8)	Mobility of ions from flames.
M. de Broglie.....1909	4.5	Smoke of cigarettes. Formula of Einstein.
J. Perrin 1909	4.11	From the distribution of particles. $N = 70.5 \cdot 10^{22}$
	4.05	From the Brownian movement $N = 71.5 \cdot 10^{22}$
	4.50	From the rotation of particles $N = 65 \cdot 10^{22}$
R. A. Millikan 1910	4.66	Single drops in electric field $2e = 8.60\text{-}10.07$, $3e = 13.45\text{–}13.99$. $4e = 17.46\text{–}19.10$. $5e = 22.52\text{–}24.14$. $6e = 26.89\text{–}29.82$.
F. Ehrenhaft.....1910	0.9–12.4 (Pt) 0.9–26.7 (Ag) 0.5–9.6 (Au) 0.5–28.9 (P)	Occurrence of maxima of frequency in the distribution of individual charges.
K. Przibram.....1910	3.45 (O) 4.2 (air) 4.15 (HCl) 4.7 (P).	Distances of maxima of frequency in the distribution of individual charges.

It seems very difficult to explain the deviations observed by Ehrenhaft and Przibram from the atomistic theory of electricity.* The accuracy of the law of Stokes

*After this had been written, some very important memoirs of Millikan and of Perrin and his collaborators, Roux and Bjerrum, have ap-

has been very thoroughly investigated and confirmed in similar cases, so that a deviation from it of the necessary magnitude seems unlikely. Further, through such an expectation all the former measurements indicating the atomic division of electricity would become invalidated. It has however been observed in many cases that exceptions from Stokes' law occur with particles which are not spherical, for instance, with the crystalline particles of sal ammonia. Other deviations from this law occur with very minute spheres. As matters stand at present the proof of the granular or atomic distribution of matter rests chiefly on the observations of the movement of small suspended particles in a surrounding liquid. A system of this nature is called a colloidal solution; in the experiments cited above the particles were very coarse.

It is a matter of great interest, that the celebrated mathematical physicist Planck has tried to introduce an atomistic view of the radiant energy. Thus a body emitting radiant heat should not lose its energy continuously but in discrete portions, which are constant for radiated energy of the same wave-length, but are in general inversely proportional to this quantity. Stark has endeavored to confirm this theorem of Planck by showing that canal rays do not emit a particular type of radiation until they have reached a certain velocity, *i. e.*, possess a sufficient quantity of energy. Other experiments of Ladenburg regarding corpuscles emitted by bodies exposed to ultraviolet light seem also favorable to Planck's hypothesis. This theorem of the

peared. They have subjected Ehrenhaft's and Przibram's experiments to a severe criticism, and they find a quite constant value of e. Millikan gives $e = 4.9 \cdot 10^{-10}$ and Perrin $e = 4.2 \cdot 10^{-10}$.

discrete structure of energy depends entirely upon that of the atomic distribution of electric charges, and it will therefore be our first problem to clear up the question raised by Ehrenhaft, before we try to give an answer to the much more difficult problem raised by Planck, whose theory has been recently attacked by Sir J. J. Thomson, who gave a wholly different explanation of the phenomenon observed by Ladenburg.

In a very interesting manner Svedberg has also shown that molecules of a real solution, namely of polonium chloride, are in constant motion and exactly of the order of magnitude demanded by theory. The number of α-particles emitted by a solid radioactive substance in unit time is not constant but changes according to the theory of probability. If n is the mean value of this number, the relative mean deviation d from this number is proportional to $1/\sqrt{n}$ according to a theory given by v. Schweidler. This theorem was verified by Regener.

If we investigate a dissolved radioactive substance and with the microscope observe the α-particles emitted in unit time from a given volume of the solution by means of the scintillations produced on a screen of zinc sulphide, then the variation of n must be greater than in a solid preparation, because the molecules are moving out of and into the observed volume. If the relative mean deviation from the mean number of radioactive molecules due to this mobility is d_1—d_1 may be calculated from a theoretical formula of v. Smoluchowski —then the total relative variation D due to the two circumstances is according to the theory of probabilities $D = \sqrt{d^2 + d_1^2}$.

Svedberg once observed a solid preparation of a polonium deposit on copper, another time a solution of polonium chloride. He found for the solid preparation $d = 42.3$ per cent. instead of the calculated number 42.8 per cent., when n was 0.559 per second. For the solution he found when

$n = 0.476$	0.349	0.224
$D_{obs} = 55.3$	71.5	83.4
$D_{calc} = 58.6$	68.8	80.5
$d_{calc} = 46.4$	54.1	67.6

The agreement between the observed and calculated values of D is very good, and the difference from the calculated values for immobile molecules (d calc.) is rather great, so that the movement of the dissolved molecules seems to be well proved.

Through these many measurements of different kinds and especially through the study of the Brownian movement, the law of Avogadro, that a given number of molecules of any gas at a fixed temperature and pressure (*e. g.*, 0° C. and 1 atmosphere) fill the same volume (under the conditions mentioned, 22,410 cm. for 2 grams of hydrogen or one grammolecule of any gas), is supported and the difference between atom and molecule which had been foreseen by Gassendi and established by Avogadro, is thereby proved to be real. And furthermore the kinetic theory of matter has been demonstrated. The use of equivalent weights instead of atomic weights which prevailed in French literature on chemistry a few years ago and which was actuated by a doubt regarding the real existence of molecules, has no longer any adherents.

It is very curious that Dalton in his "New System of Chemical Philosophy" (1808) repudiated the law of

Avogadro, published three years later. Dalton says, "At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous . . . But . . . I became convinced, that different gases have *not* their particles of the same size." In another place he says, "No two elastic fluids, probably, have the same number of particles, either in the same volume or the same weight." To Gay-Lussac's law of the simple proportions of the volumes of combining gases he objects: "In no case, perhaps, is there a nearer approach to mathematical exactness, than in that of one measure (volume) of oxygen to two of hydrogen (when they combine to form water); but here the most exact experiments I have ever made gave 1.97 hydrogen to 1 oxygen."

It is a great pity that Dalton objected so strongly to the validity of what we now call Avogadro's law, for otherwise he would have given a much more perfect atomic theory and probably the progress of science would have gone on more rapidly than it did a century ago.

LECTURE III.

SUSPENSIONS.

THROUGH the work of Perrin it has been proved that small particles which without difficulty may be observed through an ordinary microscope behave as molecules in a gas. Further Svedberg made out experimentally that the molecules in a liquid, namely a solution of polonium chloride, which are much more nearly related to those of a gas behave in quite the same manner.

Fluids containing suspended particles have attracted a very great interest in recent times; therefore a short review of their properties will be very appropriate in this place.

There are many methods of preparing such suspensions. The simplest one consists in dissolving in alcohol a substance, *e. g.*, mastich, which is insoluble in water, and pouring a quantity of this solution into water. Then the alcohol is taken up by the water and the particles of mastich remain as a mist floating in the water. Another very simple method is to grind some substance to a fine powder and throw it into a fluid which does not dissolve it, *e. g.*, kaoline with water. Other methods are founded on chemical properties. If sulphuretted hydrogen (H_2S) is introduced into an aqueous solution of arsenious acid (As_2O_3) a formation of arsenious sulphide (As_2S_3) occurs and this remains suspended in the fluid. The superfluous

H_2S may be removed from the fluid by bubbling an indifferent gas through it. In a similar manner a suspension of sulphide of antimony (Sb_2S_3) may be prepared. In other cases sulphuretted hydrogen is introduced into a dilute solution of a metallic salt (for instance salts of iron, cobalt, nickel, palladium or platinum), and a sulphide is formed, which remains partially suspended in the liquid. At the same time the acid of the salt is set free; to remove it the solution is placed in a dialyser, which allows the acid to pass through but not the suspended grains. In an analogous manner it is possible to prepare suspensions of nearly all insoluble salts. Some salts, *e. g.*, ferric acetate (Graham) or thorium nitrate are hydrolysed into hydrate and acid by the solvent water and then the hydrate often remains in suspension if the acid is dialysed away. This fact that suspended particles may be separated from salts by means of dialysis is the reason why the name of colloids has been given to them. Graham had as a matter of fact (1862) called substances such as glue, egg-albumen, gum-arabic, etc., which do not pass through parchment-paper colloids (from kolla, glue) in contradistinction to crystalloids, which pass easily through the membrane. But the suspensions have very little similarity to glue or albumen and therefore the name of colloid should be rejected in this special case.

Another method of preparing suspensions of noble metals was introduced by Bredig. He dipped two rods of the metal into water and connected the free ends of the rods with a powerful electrical machine. Then an electric arc was formed between the rods,

when these were brought near to each other. The metals evaporated and condensed to a fine dust which remained to some extent suspended. It gave a characteristic colour to the liquid, greenish brown for silver, dark brown for platinum and red or blue for gold (the blue colour corresponds to coarse particles). This method cannot be used for common metals as they react with the water. But in other liquids such as alcohols, ether, esters Svedberg succeeded in preparing suspended ordinary metals by using alternating currents.

The physical properties of such suspensions may be regarded as an arithmetic mean between those of the surrounding fluid and of the suspended matter. As the latter is generally present only to a very small extent, the general physical properties are very similar to those of the liquid. As the colour of the suspended particles, especially for metals, is strongly marked the suspension has generally a characteristic colour. Svedberg found that this colour for alkali-metals suspended in ether is very similar to that of their gases. The suspensions are opaque and show the so-called phenomenon of Tyndall, *i. e.*, if a strong beam of light falls upon them, it illuminates the suspended particles and its path may be seen from the side. This reflected light is polarized. It gives consequently a means of detecting the particles, even if they are so small that they cannot be seen with the aid of a microscope (droplets of a diameter less than about 0.0002 mm.). This is effected by the ultramicroscope, which was independently invented by Siedentopf and Zsigmondy in Germany and by Cotton and Mouton in France. In this

instrument a beam of strong light is directed through the suspension, so that its particles become illuminated. They are then observed by means of a microscope in a direction perpendicular to that of the beam of light. In this manner particles of not more than 0.000006 mm. may be detected, when they are illuminated by solar light. If the total quantity of suspended matter is known and the number of particles counted the mean diameter of each particle may be determined. It is usually assumed that the particles are of a spherical form.

The particles may be of still smaller dimensions than 0.000006 mm. They are then invisible with the strongest illumination which we can produce. Yet sometimes even then a weak Tyndall-phenomenon may be observed.

These suspensions are often called sols. In many cases the suspended particles retain with remarkably strong attraction a certain quantity of the solution from which they were precipitated. This is for instance the case with iron hydrate, which adsorbs chlorine ions from the surrounding solution of $FeCl_3$.

The suspended particles are subject to the Brownian movement and this circumstance causes them to diffuse to a certain extent. If the particles are coarse as in the cases studied by Perrin, their concentration was observed to decrease very rapidly upwards. Thus their number in the same volume decreased to one half, with an increase over a height of only 0.03 mm. The diameter of the particles was 0.00042 mm. In a height of 1 mm. the concentration decreases in the proportion of about ten thousand millions. Hence one may say

that the main amount of the fluid is wholly free from these particles. But smaller particles subside very slowly and may remain suspended in the fluid for an unlimited time. With extremely minute particles of gold Svedberg measured the diffusion colorimetrically and found its constant at 17° to be 0.27 per day, whereas the corresponding constants for H_2, O_2, Cl_2, Br_2 and I_2 in water were 3.75, 1.62, 1.22, 0.8 and 0.5 respectively. The gold-emulsion was prepared according to a method given by Zsigmondy, the so-called phosphorus-method. Zsigmondy estimates the diameter of the particles, which cannot be seen with the ultra-microscope, to be a millionth millimeter, Svedberg calculated it from the rate of diffusion according to a formula of Einstein to the magnitude 0.94 millionths of a millimeter. The corresponding values for H_2, O_2, Cl_2, Br_2 and I_2 are according to the formula of Einstein 0.06, 0.20, 0.20, 0.32 and 0.52 respectively in the same units. Obviously the difference from a real so ution is in this case not very great. It is evident that currents produced by the slightest inequality of temperature may disturb these observations.

As early as in 1809 Reuss in Moscow observed that small suspended particles in a fluid are moved by an electric current. This indicates that they carry a certain electric charge. The surrounding fluid is charged with the opposite electricity and is therefore carried in the opposite direction by the current. According to a rule formulated by Coehn the substance with the greater dielectric constant is charged positively. Water has a higher constant than most other substances and is therefore generally charged positively and the

suspended particles negatively. Some few substances are exceptions, especially oxides such as those of iron, zinc, cobalt and aluminium, also carbonate of baryta, hydroxides, etc.

If we have water in a narrow glass tube with two electrodes, between which a current is carried, the water is carried along with the current. The same is the case if a current traverses a porous diaphragm, which may be regarded as a system of capillary tubes through which the water is pressed. This curious phenomenon was observed at a very early stage as such porous diaphragms are used in galvanic cells. The strength of such a current is easily measured by means of the height to which the fluid can be pressed up or by means of the quantity of fluid transported.

The velocity with which suspended particles move under the influence of the electric current is proportional to the potential-gradient, just as the movement of ions is. This velocity of the particles is therefore reduced to that which would be found if the potential gradient were 1 volt per cm. There have been found different values lying between about 10.10^{-5} and 40.10^{-5} cm. per second, about the same as for ions. (The corresponding velocity at 18° C. is for Li-ion 36.10^{-5} for K-ion 66.10^{-5}).

The particles are charged to a certain potential above or below that of the surrounding fluid. It is of the same sign as the charge and proportional to it and inversely proportional to the radius of the particle. This potential reaches a value of some centivolts. If now the radius of the particle is doubled, the charge must be doubled in order to give the same difference of

potential. The driving force is (if the potential gradient remains constant) proportional to the charge, therefore proportional to the radius. But on the other hand according to Stokes' law the friction increases proportionally to the radius and the velocity. (Stokes' law is not absolutely exact for such small particles, see p. 32). Therefore the velocity remains the same independently of the radius of the particle, a fact which agrees well with experiment. On this ground the velocity would remain unaltered if the dimensions of the particles decreased to molecular magnitude. This circumstance, combined with the similar magnitude of the mobility of ions and particles, indicates that the suspended particles may to a certain degree be regarded as ions of very great dimensions.

Experiments on electric endosmose as well as on the electric traction of suspended particles indicate that the charge of the suspended substance is in a high degree dependent on electrolytes present in the water. Acids and bases especially exert a great influence, their hydrogen or hydroxyl ions being adsorbed by the solid particles. As the latter are generally negatively charged, they may by means of the hydrogen ions be charged positively, so that the direction of motion of the fluid and particles is changed. The influence of the ions increases with the quantity of acid or base added, so that it is possible to gradually alter the charge of the suspended particles or of the diaphragm (in osmotic experiments) from negative to positive.

Of other ions, the monovalent ones have a much smaller effect than the bivalent ones, the latter a smaller effect than the trivalent ones. The suspended

particle adsorbs with preference those salt-ions which have a charge opposite to its own. Therefore the movement of the particles is generally hampered by addition of salts and especially of such salts as possess polyvalent ions of a charge opposite to that of the particle. Sometimes it may happen that in such cases the final total charge is the opposite of that of the particle in water alone, just as in the addition of acids. Thus Burton found that a 0.005 normal solution of $Al_2(SO_4)_3$ was sufficient to neutralize the negative charge of suspended silver-particles, so that in higher concentrations of the aluminium-sulphate the silver-particles migrated in the direction of the current.

Electrolytes have another influence upon suspensions. It was very well known to geologists that suspended particles carried out into the sea subside much more rapidly in salt than in fresh water. Barus investigated very thoroughly the influence of different substances and showed that non-electrolytes have no influence, acids and salts of heavy metals on the contrary a very great one. This has been verified by Bodlaender who found that with kaoline-powder in water, a concentration of 0.0001 normal $ZnSO_4$ causes subsidence in about the same degree as a 0.00015 normal solution of sulphuric acid and as a 0.003 normal solution of ammonium chloride. Alkalis have hardly any action. As a general rule it may be said that acids and polyvalent positive ions exert the greatest action. (The rule has some very peculiar exceptions in phosphoric, tartaric and oxalic acids, but not in the very much weaker acetic acid; a redetermination seems therefore very desirable).

Similar experiments have been performed by Bechhold and others. The former found that the following quantities (in equivalents) of different electrolytes exert the same action in precipitating emulsions of mastich:

$HgCl_2$	∞	$CaCl_2$	50	$CdSO_4$	25	CuN_2O_6	5
KOH	∞	CaN_2O_6	50	$Ni(CH_3CO_2)_2$	25	$Cu(CH_3CO_2)_2$	5
NaCl	1000	$Ba(OH)_2$	50	HCl	10	$HgNO_3$	1.25
CH_3COOH	500	$BaCl_2$	50	H_2SO_4	10	$FeCl_3$	1
$Ag\,NO_3$	125	BaN_2O_6	50	$PtCl_4$	10	FeN_3O_9	1
$MgSO_4$	100	ZnN_2O_6	50	$CuCl_2$	10	$Al_2(SO_4)_3$	0.5
MgN_2O_6	100	CoN_2O_6	50	$CuSO_4$	10	AlN_3O_9	0.5
$ZnSO_4$	100	NiN_2O_6	50	PbN_2O_6	5	$Fe_2(SO_4)_3$	0.5

The anions seem to exert a very insignificant influence. The alkalis have no influence and the same holds for the feebly dissociated mercuric chloride (a peculiar case since $HgNO_3$ has a very strong action). The salts of monovalent metals act much less than those of bivalent metals, to which silver approaches very closely. A still more powerful action is characteristic of the strong acids (not of the weak acetic acid). Some few nitrates and acetates act more strongly than even the strong acids and by far the greatest action is exerted by the trivalent positive ions.

Rather many irregularities, which still await their explanation, are found, but in general it seems as if the discharging property of the ions had the greatest influence on the negatively charged mastich-droplets.

According to experiments of Whitney and Straw, the hydroxyl-ions seem to favor the suspension of certain substances, such as turpentine, carvene, kaoline, soot and silver.

Similar experiments have been carried out with the negatively charged suspension of arsenious sulphide.

The greatest action was found to be exerted by trivalent positive ions, an intermediate position was held by divalent and the weakest action was due to monovalent positive ions. In this case the hydrogen ions did not differ so very much from potassium-, sodium- or lithium-ions. On the other hand some organic positive ions such as those of aniline, toluidine, morphium and fuchsine had an abnormally great action, sometimes greater than that of divalent ions. Negative ions exert no appreciable influence.

In exactly the opposite way the ions react with a positively charged sol, as the following experiments by Freundlich on Fe $(OH)_3$ suspension indicate. Hardly any influence at all was exerted by hydrochloric acid. The quantities of different salts required to give a precipitate were the following (in millimoles per litre):

HCl	> 400	NaCl	9.25	$MgSO_4$	0.217
KI	16.2	KCl	9.03	K_2SO_4	0.204
KBr	12.5	$\frac{1}{2}Ba(OH)_2$	0.42	$K_2Cr_2O_7$	0.194
KNO_3	11.9	H_2SO_4	about 0.5		
$\frac{1}{2}BaCl_2$	9.64	Tl_2SO_4	0.219		

The bases (BaO_2H_2) rank here with the salts of divalent anions (SO_4 and Cr_2O_7); a far smaller influence is exerted by the salts of monovalent ions and the monovalent acids give an exceptionally low effect. Also organic anions are much more effective than inorganic ones, according to Linder and Picton. The hydrogen ion has a suspending power for positively charged suspensions.

The rule of the greater effectiveness of polyvalent ions was first found by Schulze in 1882; his experiments dealt only with sols of As_2S_3 and Sb_2S_3; but this rule has been verified in all the cases thoroughly examined by the following investigators.

The chemical behavior of suspended particles of noble metals was very thoroughly examined by Svedberg and his pupils. Just as spongy platinum destroys hydrogen peroxide, so platinum sol has the same effect, but in a still higher degree corresponding to its fine division.

Bredig and Mueller von Berneck shook together fulminating gas and 2.5 c.c. water containing about 0.17 milligrams of suspended platinum and found that the reaction went on with constant velocity, as was quite natural, since the concentration of fulminating gas always remained the same throughout the shaking. The combined quantities are seen in the following figures (valid at 25° C.):

Time Minutes.	Combined Gas c.c.	Velocity c.c. per Min.
10	17.8	1.78
20	35.8	1.80
30	54.8	1.90
40	72.4	1.76
50	90.2	1.78

After two weeks, during which this liquid had been shaken in the day-time with a total resulting combination of about 10,000 c.c. of fulminating gas, it was tried again and found to cause 98.2 c.c. of fulminating gas to combine in 50 minutes. The effectiveness of the platinum-sol had therefore not diminished.

They then investigated the decomposition of hydrogen peroxide in neutral or weakly acid (through an addition of $\frac{1}{2000}$ c.c. NaH_2PO_4) solution. They found that the reaction was of the monomolecular type, *i. e.*, that the quantity of H_2O_2 decomposed per minute was proportional to the concentration of H_2O_2, as was to be expected.

A totally different set of relations is obtained if sodium hydrate is added. With increasing quantity of the hydrate the velocity of reaction at first increases, then reaches a maximum when the solution is about 0.02 normal in regard to the alkali, and afterwards it decreases again if the concentration of the latter is further increased. This is evident from the following figures, which indicate the time which is necessary for decomposition of $\frac{1}{42}$ normal H_2O_2 to its half strength. The quantity of platinum was always the same, $\frac{1}{800000}$ normal.

Conc. of NaOH.	0	1/512	1/256	1/128	1/64	1/32	1/16	1/8	1/4	1/2	1
Time in minutes	255	34	28	24	25	22	34	34	70	162	520

Here the rate of decomposition is for low concentrations of NaOH almost independent of the concentration of H_2O_2, whereas at higher concentrations of NaOH the reaction follows the monomolecular formula, *i. e.*, the rate is proportional to the concentration of H_2O_2 as is seen from the following figures (valid at 25° C.).

1/512 *n* NaOH.

Time.	$a-x$	k_1	k_0
0	23.9	—	—
6	22.4	0.0047	0.25
15	19.65	0.0057	0.28
25	16.5	0.0064	0.30
40	11.17	0.0083	0.32
55	6.35	0.0105	0.32

1/128 *n* NaOH.

Time.	$a-x$	k_1	k_0
0	23.83	——	—
6	21.15	0.0086	0.45
15	16.67	0.0104	0.48
25	11.6	0.0125	0.49
40	5.33	0.0153	0.46

1/32 n NaOH.

Time.	$a-x$	k_1	k_0
0	23.9	——	—
6	20.02	0.0128	0.65
15	15.4	0.0127	0.57
25	10.9	0.0136	0.52
40	6.13	0.0148	0.44

$a-x$ is the quantity of H_2O_2 present, determined by titration. k_1 is the constant giving the velocity of reaction according to the monomolecular formula, k_0 on the other hand the velocity of reaction, calculated on the supposition of a constant rate from the beginning.

In the first instance (1/512 n NaOH) k_1 increases in the proportion 1 to 2.25 during the time of reaction. Even the quantity k_0 is not absolutely constant, but shows an obvious tendency to increase with time. The second case (1/128 n NaOH) gives almost the same behaviour, but k_0 is very nearly constant. In the third instance k_1 increases slightly (about 15 per cent.) with time, so that the reaction proceeds almost as a monomolecular one; on the other hand k_0 decreases by about a third of its original value.

Similar irregularities are often found in the investigation of the catalytic action of ferments; and therefore Bredig calls platinum-sol and similar substances inorganic ferments. A maximum effect in the presence of a certain quantity of sodium hydrate has been observed by Jacobson for the decomposition of H_2O_2 by means of emulsin, pancreatic juice and malt-ferment. In the inversion of cane-sugar by means of invertin the maximum effect is attained if a certain quantity of acid is present. In this case also the quantity of cane sugar decomposed in unit time is nearly independent of the concentration of the sugar, if this exceeds 2 per cent.,

but at very low concentration (below 0.5 per cent.) the rate of inversion follows the monomolecular formula.

The similarity between ferments and platinum-sol is still more strikingly manifested in the fact that in each case their action is paralysed by the presence of very small quantities of "poisons." Hydrocyanic acid, carbon monoxide, iodine, mercuric chloride, hydrogen sulphide, etc., exert such an action on platinum-sol. The first-mentioned has a very peculiar action; at first it paralyses the sol, but later on this recovers and has an even greater effect than without the poison. A similar recovery of emulsin and of pancreatic ferment after their paralysis by HCN has been observed by Jacobson.

In these changes, the reacting substances probably condense upon the finely divided metallic particles, as we shall see in the next chapter, and in such condensed systems the chief reaction takes place. This is probably the case with many gas-reactions in the presence of finely divided platinum, for instance, the oxidation of SO_2 by means of oxygen to SO_3, which has been examined by Fink. Wallach found that the terpenes and their derivatives may easily give addition-products with hydrogen in the presence of finely divided palladium, prepared according to Bredig's method (cf. next chapter), which is known to condense hydrogen on its surface very strongly. Evidently the organic substances are also concentrated around the palladium particles and in these surface-layers the reaction takes place. These reactions proceed just as if the reagents were subjected to a high pressure, which is also favorable to them

The magnitude of the suspended particles is highly dependent upon the concentration of the solutions from which they are precipitated, as Biltz in particular has proved. On this magnitude the optical properties of the suspension, color and translucence, which are caused by diffraction of the light, depend. Thus Schulze as early as 1882 observed that if he prepared two suspensions of As_2S_3 the one from a concentrated, the other from a dilute solution of As_2O_3 by leading in H_2S (cf. p. 36), and then diluted the former until the concentration of As_2O_3 was the same as in the latter, the suspension containing the coarser particles were less translucent and possessed a clearer yellow colour, than the yellowish red suspension of finer particles. Svedberg subjected this peculiarity to a closer investigation. He used, for instance, the method of reducing gold from its chloride by means of chlorhydrate of hydrazin and obtained the figures given in the following table, where c is the concentration (normality) of the solution of gold chloride ($AuCl_3$) used and k the depth of its colour determined by dilution until the colour was not longer perceptible.

c	k	m	Colour
$50{,}000 \times 10^{-7}$	2,000	343	bluish grey.
21,000	5,000		blue.
10,000	75,000		blue.
7,500	200,000	37	
6,000	250,000		fuchsin red.
3,300	200,000	20	"
1,700	125,000		"
1,000	100,000		"
500		13	"
200	50,000		"
15	17,000		"
7	25,000		"

The intensity k of the colour of solutions containing the same quantity of gold at first increases when the gold particles diminish and thereafter decreases. The diameter of the particles, in millionths of a millimeter is tabulated under m; it diminishes rapidly with c, and at the same time the colour changes. Emulsions containing still smaller particles of gold reduced by means of an ethereal solution of phosphorus (Zsigmondy's method) are ruby red to reddish yellow according to the fineness of the particles. This last column reminds one of that of gold chloride, which has a value of $k=5{,}000$. Similar maxima of k although not so strongly marked have been obtained by Svedberg for suspensions of $Fe(OH)_3$ and of As_2S_3.

If a solution of phenol in water is cooled, droplets of phenol separate out and two coexisting phases are formed. Similarly when a solution of gelatine is cooled it gives a solid jelly which after all consists of two different phases, one of gelatine with a small percentage of water and one of water with a small content of gelatine, as Buetschli at first demonstrated as probable.

Similar properties are found with some emulsions, and especially with those of sulphur prepared according to Rappo by allowing a saturated solution of sodium thiosulphate to drop into cold concentrated sulphuric acid. Rappo found that this emulsion is precipitated by the addition of certain salts such as NaCl, KNO_3, KCl, Na_2SO_4 or K_2SO_4, although NH_4-salts do not seem to possess this power. The precipitates made by means of sodium salts, dissolve in increased quantities of water or at higher temperatures.

Svedberg and his pupil Odén investigated this phenomenon. They found that the solubility of this sulphur increased with temperature approximately according to an exponential law, which holds good also for the change of solubility of other substances with temperature. From this it is possible to calculate the heat of solution of the sulphur (cfr. Lecture V) and in this manner I have found the following values per grammolecule:

Normal	Cal.	Solubility at 20°
in 0.2 NaCl	42,400 (between 14.8° and 25.0°)	14.1%
in 0.3 NaCl	22,000 (between 16.5° and 38.5°)	1.2
in 0.4 NaCl	33,100 (between 23.1° and 47.5°)	0.3
in 0.5 NaCl	33,400 (between 31.9° and 41.8°)	0.08
in 0.2 NaBr	36,600 (between 14.9° and 19.7°)	11.0
in 0.2 (mol.) Na_2SO_4	42,500 (between 13.9° and 22.6°)	4.1

The experimental errors are very great, so that the calculated values of the heat of solution may be regarded as agreeing rather well with the mean value 36,200 cal., an unusually high value for a heat of solution.

The figures giving the solubility at 20° indicate that NaCl and NaBr have nearly the same influence on the colloidal sulphur, while Na_2SO_4 has a greater influence than NaCl if in equimolecular, but less influence if in equivalent solution.

Odén has investigated this last property more fully. He finds that different preparations of suspended sulphur behave rather differently, and this explains the irregularity in Svedberg's figures. He finds that if the solubility of the sulphur (in per cent.) at 16° C. is represented by S and the normality of the NaCl by n then the following experimental formula holds good:

$$S = 32{,}810\ (100n)^{-2.8}$$

as is seen from the following figures:

n	Sobs.	Scalc.	Diff.
0.21	5.43	6.51	−1.08
0.34	1.68	1.69	—0.01
0.46	0.74	0.73	+0.01
0.58	0.36	0.38	−0.02
0.74	0.07	0.19	−0.12

Different salts have very different powers of causing precipitates. The following figures give the inverse values of the quantities in gram equivalents per liter, which must be added in order to produce precipitation. The solutions lose their transparency at a certain concentration, which may be determined rather accurately. The inverse value of their concentration in gram equivalents per litre is given below:

LiCl	1.1	KCl	47.5	$MgSO_4$	54	$ZnSO_4$	6.6
NH_4Cl	2.3	K_2SO_4	39.7	MgN_2O_6	63	CdN_2O_6	10.2
$(NH_4)_2SO_4$	1.7	KNO_3	45.5	$CaCl_2$	123	$AlCl_3$	76
NH_4NO_3	2.0	RbCl	63	CaN_2O_6	124	$CuSO_4$	51
NaCl	6.1	CsCl	108	SrN_2O_6	193	MnN_2O_6	53
Na_2SO_4	5.7			$BaCl_2$	238	NiN_2O_6	11.2
$NaNO_3$	6.1			BaN_2O_6	231	$UO_2N_2O_6$	36.5

An addition of acids increases the stability of the suspension, so that much greater concentrations of the salts are needed in order to produce precipitation, than if the acid is not present. HNO_3 and H_2SO_4 have the greatest influence, HCl and HBr much less, about 60 per cent. of that of HNO_3 or H_2SO_4 in equimolecular solution. This so-called dispersing action increases till it reaches a maximum at a certain concentration and thereafter it diminishes again. Formic acid has about 14 times less action than HNO_3 or H_2SO_4 in concentrations below normal. It does not possess a maximum

of action at any concentration. Acetic acid possesses a very small activity in this respect.

It seems very difficult to draw general conclusions from all these figures. In groups of similar salts, as for instance the salts of the alkali-metals, the precipitating influence of the salt increases very rapidly with the atomic weight of the metal, and metals of a high valency generally have a greater influence, but the regularity is not very pronounced.

LECTURE IV.

THE PHENOMENA OF ADSORPTION.

In the year 1777 two chemists, the German, R. Scheele and the Italian, F. Fontana independently discovered that charcoal has a great tendency to take up and retain gases from its surroundings. This phenomenon was then studied by a great number of scientists, amongst whom the renowned French savant Saussure (1814) deserves special mention. In 1791 Lowitz found that charcoal is also able to take up coloring matter from solutions, so that a complete decoloration of fluids could be brought about by simply filtering them through carbon, a method which is of the greatest value for many industrial processes. Payen afterwards showed that a great number of salts and other substances were condensed upon charcoal. In further investigations it was discovered that not only carbon but even other substances, which are finely divided or consist of agglomerations of fine fibres, such as finely divided platinum, iridium, powdered glass or glass-wool, powdered silicic acid, clay, kaoline, metastannic acid, meerschaum, asbestos, paper, cotton, leather, silk or wool possess the same attracting or condensing power as charcoal.

On this property of fibres of mineral, vegetable, or animal origin many dyeing and tanning processes depend; further the retention of carbonic acid, moisture and salts necessary for the vegetation in different soils

as well as the hygroscopic nature of various materials are consequences of adsorption processes. Clearly they are of the greatest practical importance and they have therefore attracted the keen interest of many investigators.

The chief problem, which these investigators have had in view, was to determine how great the quantity taken up by the porous substance was, and how it changed with the concentration of the surrounding gas or solution and with the temperature. The phenomenon itself is according to a suggestion by E. du Bois Reymond called "adsorption," which is meant to indicate that the "adsorbed" substance does not enter into the interior of the "adsorbent," but is only attracted to its surface, in contradistinction to solution (especially solid solution) or chemical interaction. These two latter processes sometimes accompany adsorption and so exert a disturbing influence.

It was found, as one would expect, that the adsorbed quantity increases with the concentration of the surrounding gas or solution. In some cases there exists a proportionality, reminding one of the law of Henry, for instance, with gases in general at high temperatures and with hydrogen and helium even at rather low temperatures (− 80° C.). But in the majority of cases the adsorbed quantity increases much more slowly than the concentration considered, and this was expressed by means of a formula, which has often proved very useful in interpolations, namely,

$$a = kc^n,$$

where a is the adsorbed quantity per g. of adsorbent, k

a constant (the adsorption constant), c the pressure of the surrounding gas or the concentration of the surrounding liquid studied and finally n is an exponent less than unity.

The formula was controlled by giving it the form

$$\log a = \log k + n \log c$$

and plotting log a against log c as abscissa. The points thus determined were joined together by a curve, which ought to be a straight line if n is constant, as it was generally found to be (cf. diagram p. 66). As examples the following figures may be given:

ADSORPTION OF CARBONIC ACID ON CHARCOAL AT 0.° $n = 0.333$; $k = 2.96$ (Travers).

c	a (observed).	a (calculated).
0.41	1.94	2.21
2.51	3.94	3.99
13.74	7.65	7.00
41.64	10.49	10.1
85.86	12.97	12.9

Here, as is usually the case with gases, the concentration is expressed as gas-pressure in cm. of mercury; a in cubic centimeters (at 0°, and 76 cm.) of the adsorbed gas on one gram of the adsorbing substance. In this case the value of a at low pressures falls a little short of the calculation, *i. e.*, the straight line is bent down somewhat towards the abscissa axis. This phenomenon is general with gases at low pressures.

ADSORPTION OF ACETIC ACID ON CHARCOAL AT 14° $n = 0.25$; $k = 2.112$ (G. C. Schmidt).

c	a (observed).	a (calculated).
0.0365	0.93	0.923
0.084	1.15	1.137
0.135	1.248	1.282
0.206	1.43	1.423
0.350	1.62	1.625

The agreement between the observed and the calculated values is in this case very good. Many similar cases were investigated and on the whole it may be said that the calculated values were in good accord with the observed ones. It was therefore generally assumed that the equation above represents the adsorption phenomenon at constant temperature, *i. e.*, gives the so-called adsorption-isotherm. As will be seen later on, this hypothesis is rather far from the truth, and when we look critically at the tabulated observations we find in most cases, that the intervals in which the values of a have changed are very limited, as for example, in the last case between 0.93 and 1.62, *i. e.*, not fully in the proportion 1 to 2.

With regard to the influence of temperature, it was found to be rather insignificant for the adsorption of substances from their solutions especially at higher temperatures, as Freundlich showed. With gases the constant k decreased exponentially with increasing temperature and n increased with temperature in the manner indicated by the following figures for the adsorption of carbonic acid on charcoal according to Travers's measurements.

t	k (observed).	k (calculated).	n
− 78°	14.29	16.62	0.133
0°	2.96	2.96	0.333
35°	1.236	1.364	0.461
61°	0.721	0.768	0.479
100°	0.324	0.324	0.518

The calculated values of k are found by means of the following formula:

$$\log k_t = \log k_0 - 0.009608\, t$$

where t is the temperature in centrigade degrees and the logarithms are to the base 10.

If the temperature were increased sufficiently n would approach very near to 1; on the other hand at very low temperatures approaching to absolute zero n takes values decreasing very nearly to 0.

The exponential formula given above indicates that the adsorbed quantity should increase to infinity if the pressure or osmotic pressure of the examined substances were to increase without limit. This was also believed to be the case until quite recently G. C. Schmidt found some cases (adsorption of acetic acid or of iodine on carbon) in which the adsorption reached a very well marked maximum, S, which was arrived at asymptotically on increasing the concentration, and which could therefore not be exceeded.

He therefore proposed a new formula of the type

$$\log \frac{S}{S-a} + Aa = \frac{1}{k}c,$$

where k, A and S are constants. This formula has the weakness that it contains three constants to be determined experimentally, and this gives it only the value of an interpolation formula which may lack a higher physical meaning. If a approaches very near to S we find that the logarithmic term increases very rapidly towards infinity, *i. e.*, c must also approach infinity, *i. e.*, S is a maximal value of a.

It would increase the value of the formula to a high degree if A were zero or if it were a function of S, for then there would be only two constants and the formula might be more a rational one. Schmidt soon found that A was not zero and therefore determined it experimentally. On inspecting the values of A determined

by Schmidt I was surprised to see that the product AS was very nearly a constant namely, 0.4343, the ratio between common and natural logarithms. In general it was a trifle lower, as is indicated by the following values of S and A given by Schmidt.

		S	A	SA	System
Schmidt's Tab.	8 gives	0.88	0.55	0.484	Acetic acid, charcoal from cane sugar.
Tab.	9 "	2.48	0.1670	0.414	Acetic acid, charcoal of animal origin.
"	10 "	1.36	0.3275	0.4453	Iodine in benzene, charcoal of animal origin.
"	12 "	0.9052	0.4660	0.4218	Acetic acid, charcoal from cane sugar.
"	14 "	1.4570	0.245	0.3570	Acetic acid, charcoal of animal origin.
"	16 "	1.7829	0.2276	0.4057	Acetic acid, charcoal from cane sugar.

I therefore recalculated Schmidt's figures under the supposition that the product SA was really 0.4343 and found for instance the following results for Schmidt's Tab. 12, which may also give an insight into the real meaning of an upper limit to the adsorbed quantity.

SCHMIDT'S TAB. 12 100 C.C. ACETIC ACID WITH 10 g. CHARCOAL FROM CANE SUGAR. $S = 0.905$.

c	a	k
0.00884	0.05223	12.60
0.03217	0.1006	11.90
0.0372	0.1259	8.65
0.2116	0.3224	5.81
1.161	0.5879	6.87
3.759	0.7952	7.05
3.752	0.8105	6.34
5.602	0.8284	8.33
9.175	0.901	4.77
16.60	0.905	—
29.38	0.902	—
30.6	0.904	—

As is seen from the figures at the bottom of the table a increases very slowly with increase of c, after the latter has reached a value higher than 0.9 (grams per 100 c.c.). The three last figures for a are to be regarded as constant within the errors of observation. Schmidt therefore took a mean value of those and some other figures 0.905 (g in 10 g carbon.) as giving the limiting value which the adsorption of acetic acid might reach in solutions as highly concentrated as possible.

The value under k should be a constant, whereas it in reality changes in about the proportion 1 to 2. But as a matter of fact these discrepancies are rather insignificant. As regards the end value 4.77, the corresponding value of a (0.901) lies so very near to the limit value S (0.905) that an error in either of these values of 0.004, which might well occur would render k infinite. The second and the third observations lie very near to each other (in regard to the value of c) and ought to approximately give the same value of k. But for these weak concentrations again, a small experimental error gives a very great error in k. The third experiment gives very nearly the right value of k, *i. e.*, about the average one. We therefore conclude that k is a constant within the limits of the experimental errors. As will be seen later on it is very probable that the k-values increase somewhat with dilution just as in the case cited here.

The equation of Schmidt with $AS = 0.4343$ corresponds to a very simple differential equation, namely,

$$\frac{da}{dc} = \frac{1}{k}\frac{S - a}{a}.$$

This means that if we have a solution of the concentra-

tion c in equilibrium with charcoal every 10 grams of which carry a grams of solute and if we then increase the concentration by dc, it is sufficient to add a quantity da to the adsorbed layer in order that the equilibrium should be maintained. The equation denotes that da is zero, when $S = a$, *i. e.*, the limiting adsorption has been attained. It also denotes that da/dc is infinite for $a = 0$, *i. e.*, that on the addition of a small quantity of dissolved substance to pure water and pure charcoal, the latter takes away all the acetic acid from the solution. We also see from the figures above how c increases in a ratio nearly proportional to the square of the ratio in which a simultaneously increases. From this it follows that $c:a$ at infinite dilution is zero, as is shown by the differential equation. This corresponds also to the well-known fact, that on filtering dissolved dyes through charcoal, all the color is taken away at once, a fact which is used in practice for purifying solutions, *e. g.*, of cane sugar, etc. The analogous fact that at low temperatures charcoal adsorbs all of a surrounding gas is well known; it is to the great credit of Sir James Dewar that he has introduced this very convenient method of preparing high vacua.

As I had convinced myself that the new, highly accurate measurements of G. C. Schmidt agree very well within the errors of observation with the equation given above, I enquired next as to how gases would behave. From older investigations it was perfectly clear that they would not follow the equation in question at high temperatures.

Now there have appeared during the past year two very accurate series of measurements on the adsorption

of gases, carried out by the Russian Titoff and by Miss Ida Homfray, who worked in the laboratory of Sir William Ramsay. It seemed very probable from what they had said regarding their observations, that they had also observed a maximum charge S for gases, although they had not given such an explanation to their results. Titoff says, that at high charges of the carbon there comes a point where c increases with extreme rapidity as compared with a. For carbonic acid and ammonia at -76.5 and $-23°.5$ he observed values of a amounting to 114.1 and 154.4 c.c. per g. carbon, respectively, whereas according to the formula given above, I calculated the limiting values $S = 114.6$ and 158, respectively. Titoff had then practically reached this limit, especially in the case of carbonic acid.

As is seen from my calculations, the limiting value of S is independent of temperature and may therefore be called the constant of saturation. For carbonic acid Titoff has given two series of observations at 0°, which I quote here calculated according to the same formula as was used for the solutions. c is expressed as pressure in cm. Hg.

CARBONIC ACID AT 0° ADSORBED BY COCOANUT-CHARCOAL, ACCORDING TO TITOFF.

c	a	k
0.05	0.8491	24.9
0.32	3.4601	159
1.09	8.5059	89
2.54	15.148	60.5
8.30	27.782	52.0
17.35	39.898	48.9
31.59	50.241	52.7
45.42	56.818	56.0
58.91	61.372	58.9
70.32	64.529	61.6
75.51	65.854	62.2

Regarding the first two observations Titoff says himself that measurements in which c is less than one, are very unreliable. We therefore find here the two extreme values of k. By a chance their geometrical mean, about 63, is very near to the mean value of k. Thereafter k is nearly constant, sinking a little to begin with, and then increasing again. This last increase may be due to a small inaccuracy in the value of S and is therefore not of much importance, but the decrease of k at the beginning of the series is characteristic and agrees with the experiments of Schmidt.

I also succeeded in calculating the figures of Miss Homfray in the same manner and give below the experimental results of a series of investigations regarding methane.

METHANE AT −33° ADSORBED BY COCOANUT-COAL, ACCORDING TO MISS HOMFRAY, $S = 274$.

c	a	k
0.45	35.21	140.6
0.66	44.64	101.5
0.94	55.36	89.5
1.28	64.65	88.0
1.65	73.80	85.1
2.13	83.20	83.9
2.68	92.12	84.0
3.37	100.9	84.9
4.10	109.5	85.3

This series shows a high degree of regularity, which is partially explained by the relatively small variation of c. It gives occasion for similar remarks concerning the variation of the constant k as did the carbonic acid series of Titoff.

At higher temperatures the gases do not obey the law expressed by the formula so far made use of. This

depends upon the variation in the heat of adsorption. Titoff has made some very interesting experiments regarding this quantity. He found in agreement with some old experiments of Chappuis that the first traces of gas to be adsorbed always evolved more heat than the subsequent additions, as will be clear from the following figures, observed by means of an ice-calorimeter, *i. e.*, at 0°.

	q_0	Q_0	q_1	Q_1
Nitrogen	0.330	7392	0.210	4700
Carbonic acid	0.347	7772	0.293	6564
Ammonia	0.502	11245	0.384	9408

q_0 is the number of calories developed by one cubic centimeter of gas during its adsorption in a large quantity of carbon; q_1 is the corresponding heat developed, when the adsorption has already proceeded to a certain degree. Q_0 and Q_1 are the same figures for one grammolecule, corresponding to 22,400 cubic centimeters.

Now the second law of thermodynamics demands that

$$\frac{d \log p}{dt} = \frac{Q}{1.985\ T^2}.$$

Here p is the pressure of gas which is in equilibrium with a certain adsorbed quantity a. Therefore if Q were constant and if we plotted $\log p$ as a function of $\log a$ at different temperatures the curves so obtained for two different temperatures should be equidistant from one another for all values of p or a. But if Q is not constant but greater for low values of a, as is actually the case, then the distance between the two curves ought to be greater at lower values of a than at higher, as is really found, for instance with carbonic acid according to the measurements of Titoff, one of whose

diagrams I have reproduced here. If the curves were absolutely equidistant the whole way and our equation were valid for one of them, for instance that at 0°, then it would hold for higher temperatures, with only a change in the constant k. Now we know that at low values of a the distance will be greater than at higher values, *i. e.*, p must be too great and as k is proportional

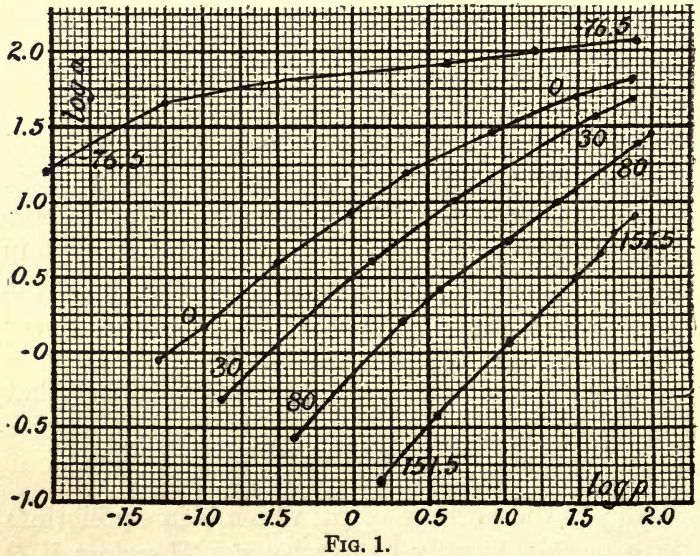

FIG. 1.

to p (or c, cf. the formula of Schmidt) k also must be too great. This is the real reason why we observe an increase of k with diminishing a and p in the tables given above. At higher temperatures this disagreement with our formula will increase more and more, the curves will become steeper and steeper. The slope of the upper curves towards the left is 26°.57, corresponding to a tangent = 0.5 and for them a is nearly proportional to the square root of p (at low values of a). The slope

of the lowest curve on its left side is nearly 45°, corresponding to a tangent = 1, indicating that p and a are proportional to each other. This proportionality is characteristic for gases at small pressures and high temperatures; for hydrogen according to Titoff the rule holds even at the lowest temperature examined (− 79) and the highest pressure (72 cm. Hg). Therefore in the diagram for carbonic acid—with the exception of helium and hydrogen, all gases examined behave in the same manner—the curves will on the left hand have a fan-like distribution with an angle of $18^{\circ}.43$. At sufficiently low temperatures even helium and hydrogen would without doubt obey this general rule.

It may be remarked here that in some cases a tangent exceeding 1 has been observed; thus for helium in one case (at − 78°) 1.68, and for methane in another case (at 182°) 1.91 and other values above 1 are to be found in nearly all series of observations, but probably they are due to accidental errors of observation.

Titoff remarked that the five gases observed by him showed a great regularity, indicating that the quantities of different gases adsorbed under a pressure of 10 cm. Hg run parallel to the values of a in van der Waals' equation, which indicate the attraction of the molecules upon one another. This is true also for the gases observed by Miss Homfray as may be seen from the table on page 68.

a gives the constant of van der Waals, A the quantity of gas adsorbed on one g. of cocoanut-charcoal at a pressure of 10 cm. Hg and at 0° C. T is the absolute critical temperature and S the maximum quantity of gas (in cm. of 0° and 76 cm. pressure) which can be

adsorbed by this amount of charcoal. It should be pointed out how well the figures of Titoff (marked T.) agree with those of Miss Homfray (marked H.); as a rule the charcoal of Miss Homfray seems to have adsorbed about 10 per cent. less than that of Titoff.

	a	A	T	S
Ethylene	0.00883	41H.	284	58
Ammonia	0.00808	71T.	403	158
Carbonic acid	0.00701	30T. 28H.	304	116
Methane	0.00367	9.4H.	178	91
Carbonic oxide	0.00280	3.2H.	133	60
Oxygen	0.00269	2.5H.	155	87
Nitrogen	0.00268	2.35T. 2.0H.	127	90
Argon	0.00259	1.67H.	154	87
Hydrogen	0.00042	0.227T.	32	—

There seems to be an exception to the rule given above, in that A is less for ethylene than for ammonia. This depends upon the fact that the ethylene was very near to its saturation point at 0° C. and 10 cm. pressure. If we take 100° C. and 3.4 cm. pressure we find by interpolation from Titoff's figures for ammonia A = 2.86 c.c. whereas Miss Homfray gives for ethylene under similar conditions A = 3.07. The exception is therefore probably not genuine, and one should take values of A for adsorbed quantities far below the limiting values S.

The parallelism between adsorption and the constant a suggested the idea that this phenomenon depends upon the attraction of the molecules of the adsorbed substance and the carbon. It then is very similar to the compression of a liquid under high pressure. In the one case through increased pressure new molecules are carried into the sphere of the molecular attraction of the carbon, in the same way in the other case, new molecules are forced into the sphere of molecular

action. Just as in discussions on capillarity, we may regard this sphere as having a definite radius; if it has not, but if the attraction decreases continuously outwards, as is probably the case, it does not make any great difference, for we have then only to consider the space around a molecule in which the molecular action reaches a certain value. The quantity contained in this corresponds to the adsorbed quantity a; it is proportional to the density of the fluid. The acting pressure is equal to the sum of the external pressure and the term a/v^2 in van der Waals' formula. From this point of view I have calculated the figures of Amagat on the compressibility of liquids and I quote the exceedingly regular figures for ethyl alcohol at 0°.

COMPRESSIBILITY OF ALCOHOL AT 0° ACCORDING TO AMAGAT, $S = 1.2729$.

c	a	k
5,081+3,000 atm.	1.1521	12,836
4,937+2,500 "	1.1355	12,838
4,775+2,000 "	1.1169	12,767
4,592+1,500 "	1.0952	12,633
4,385+1,000 "	1.0703	12,437
4,140+ 500 "	1.0399	12,126
3,838+ 1 "	1.0000	11,690

The agreement is excellent. Here k decreases with decreasing pressure in contradistinction to the case with adsorption. This depends upon the fact that the heat of evaporation is greater for the compressed fluid than for the non-compressed, and the difference is the heat of compression. The latter, Q, may be calculated according to the following formula, deduced from the second law of thermodynamics:

$$Q = 0.024\, Tp\alpha,$$

where T is the absolute temperature, p is the external pressure in atmospheres—I have taken 2000 in my

calculations—and α is the coefficient of cubical expansion from 0° to 1°. In this way I obtained the following table, where Q_0 indicates the latent heat of evaporation at atmospheric pressure, k_{2000} and k_1 the values of the constant of our equation at 2000 and at 1 atm. pressure respectively.

	S	Q	Q_0	$\frac{Q+Q_0}{Q_0}$	k_{2000}	k_1	$\frac{k_{2000}}{k_1}$
Ethyl ether	1.2642	21.2	93.5	1.227	6530	5078	1.284
Ethyl alcohol	1.2729	14.5	236.5	1.0613	12767	11690	1.092
Sulphide of carbon	1.224	15.7	90.0	1.175	9755	8700	1.121

With increasing temperature Q_0 generally decreases, Q on the contrary increases, since α as well as T does so. Therefore we might expect that the constant k would increase the more rapidly with pressure the higher the temperature, and as a matter of fact, this rule also holds good, the ratio $K_{2000} : K_1$ being 1.363 for ether at 50°, 1.106 for ethyl alcohol at 40°.4 and 1.144 for sulphide of carbon at 49°.15.

Evidently adsorption is a manifestation of molecular attraction. It has been often maintained that it is due to surface tension, and the aggregation of the adsorbed molecules to the adsorbing substance was said to diminish the surface tension. On the other hand Walden has shown that according to an idea suggested by Stefan, the surface tension of a liquid is proportional to the surface pressure, which again is proportional to van der Waals' constant a divided by v^2, where n is the molecular volume. Hence as a rule gases ought to be the more easily adsorbed, the greater the surface tension of the adsorbed layer against the gas would be, which is precisely opposite to the current ideas. Lewis also has shown that the surface tension theory of adsorption, developed by Gibbs, does not

agree quantitatively with the facts of experience. It seems therefore as if surface tension did not play the chief rôle in adsorption phenomena.

I wish only in conclusion to call attention to a peculiarity which has been observed by physiological chemists, who have investigated the adsorption of colloidal substances. They have found that in most cases the adsorbed quantity is nearly independent of the concentration of the colloid in the surrounding solution provided that the same quantity of adsorbing powder was used. (Landsteiner and Uhlirz for the adsorption of euglobulin on kaolin: Michaëlis and Rona for the adsorption of albuminoses or peptones.) This regularity seems at first to indicate that a kind of compound, in constant proportions, is formed between the adsorbing powder and the adsorbed colloid. But it is very difficult for a chemist to accept such a solution. Evidently the right explanation is that as a rule substances with the highest critical points, *i. e.*, the lowest vapor pressures possess the greatest values of a, as an inspection of the tables of Landolt-Boernstein will show. The colloids investigated possess a very low vapor tension and therefore they are strongly adsorbed, so that the limiting adsorption is nearly reached even at comparatively low concentrations, and therefore adsorption apparently occurs in nearly constant proportion to the amount of adsorbent used. Of course, the limiting value is never absolutely reached, but within the errors of observation it may already be reached at low concentrations in cases such as those mentioned. This instance is certainly not devoid of interest, for it shows that constant proportions may rule in aggregates of a rather loose nature.

LECTURE V.

THE ANALOGY BETWEEN THE GASEOUS AND THE DISSOLVED STATES OF MATTER.

It is well known to all of us that the present great advance in physical chemistry is due chiefly to the introduction of two theories, the one expressing the far-reaching analogy existing between the gaseous and the dissolved states of matter, with which follows the thermodynamic treatment of chemical equilibria in solutions, and the other indicating that salts (acids and bases are regarded as hydrogen salts and as hydrates respectively) are in solution partially dissociated into their ions. As a rule it is said that this new development came abruptly and many people believe that for this reason the merit of these theories is greatly increased. I am of quite an opposite opinion. The ideas mentioned may be found in a less fully developed state in older speculations regarding the chemical behavior of solutions and we ought to lay great stress upon this fact, for it is the most convincing proof of their soundness that they should have developed quite continuously and organically from all the results of chemical experience. Of course when they at first took form, the ideas were deduced from a rather small number of observations, so that their usefulness was not very evident and on the other hand, the conservative majority of scientists were opposed to the introduction of new notions which seemingly compli-

cated their conception of Nature. The new points of view therefore lived a latent life, being again and again indicated, until there had been collected together a quantity of experimental material sufficient to demand the explanation which they were capable of giving. At such a stage in the evolution of new ideas, a rapid propagation of them takes place under sharp opposition from the teachers of the old conceptions and in the end they receive an overwhelming support simply because of the great importance of the phenomena which they alone are able to explain.

This normal course of evolution may easily be traced for the modern theory of physical chemistry. The chief progress in it is due to the discovery that the molecules of dissolved substances behave in a manner very similar to that of gases. The laws governing the properties of gases are well known and simple; by their application to the much greater and more important group of solutions we have won an extremely valuable knowledge of the nature of solutions which play by far the foremost rôle in chemistry. At the same time the far-reaching use of the laws of thermodynamics in this new chapter gave it its strength and high value. In reality the first application of thermodynamics to the phenomena peculiar to solutions is independent of the introduction of the laws of gases in this chapter. Therefore, in the first instance, we have to treat the growth of the idea of the analogy between gases and dissolved substances as the chief progress and thereafter to regard the increasing application of the laws of thermodynamics to the doctrine of solutions as the means of making the greatest possible use of

the simultaneous concepts regarding the nature of solutions.

It is here in place to recall the interesting statement of Newton that the dissolved molecules in a solution tend to get away from each other so that they finally become distributed uniformly in the solvent.

In reality this idea gives a neat explanation of the phenomena of diffusion, which are so closely related to the force of osmotic pressure. Newton regarded this tendency of dissolved molecules as due to reciprocal repulsion of the dissolved molecules, just as the diffusion of gas-molecules may be regarded as effected by the mutual repulsion of those molecules. One might well say that the modern views regarding the analogy between gaseous and dissolved substances might well have been developed from this conception of Newton. But the time was then not ripe. The experimental knowledge of chemical phenomena was too scarce for the formulating of laws regarding them. In the year 1839 Gay-Lussac expressed opinions which possess a startling suggestion of modernity. "As the effects of affinity do not change with temperature (he would better have said change but slowly with temperature), whereas dissolution (solubility) is in a high degree dependent upon it, it is very difficult to avoid the assumption that in dissolution as well as in evaporation the product is essentially limited, at a given temperature, by the number of molecules which are able to exist in a certain volume of the solvent They are separated from this, just as gaseous molecules are precipitated by a lowering of temperature. . . . . Dissolution is therefore in a high degree connected with evaporation, namely in this

respect that both of them depend on the temperature and are subject to its variations. Hence they ought to show if not a complete identity in their effects at least a great analogy." The objection that in some cases, *e. g.*, with sulphate or selenate of sodium, the solubility-curve shows a break and sometimes a fall with increasing temperature, whereas this is not the case with the vapor-tension, is refuted by means of the assertion that at the temperature where the break occurs, the substance undergoing solution is subject to a transformation.

There is, however, a difference between a gas and a dissolved substance. "The molecules of the gas do not need a solvent to hold them in suspension in a certain volume; their mutual repulsion is enough for that purpose. On the other hand, when a solid or liquid substance is dissolved, its molecules would not remain in the limited volume if they were not united by their affinity to the molecules of the solvent."

In the same memoir Gay-Lussac criticises the theory of Berthollet according to which the precipitation of, *e. g.*, sulphate of calcium from a mixture of potassium sulphate and acetate of calcium is due to a force of cohesion (measured by the insolubility) between the molecules of the sulphate of calcium, which acts even before the substance is formed.

Gay-Lussac expressed the opinion that when the solutions of two salts of different acids and bases were mixed all the four possible salts were formed, *e. g.*, in the example above there existed in the mixed solution not only K_2SO_4 and $Ca(CH_3CO_2)_2$ but also KCH_3CO_2 and $CaSO_4$. If then one of these four is very slightly

soluble, so that the solution is supersaturated with regard to it, it is precipitated, and thereupon new molecules of $CaSO_4$ may be formed in the liquid and a further precipitate occur. In the same way, the volatility of one of the products may exert its effect, as Berthollet contended. Gay-Lussac termed "this principle of the indifference of permutation" between the acids and bases present in the salts, according to the chemical doctrines of that time, *equipollency*, and the principle has found its simple explanation through the electrolytic dissociation theory.

Shortly afterwards a Venetian professor Bartholomeo Bizio expressed similar ideas (1845). He came back to them more clearly in a paper of 1860, printed in the memoirs of the "Istituto veneto." Bellati gives (1895) an analysis of Bizio's work. He says that "Bizio regarded the dissolved substance as an elastic vapor distributed in the solvent. The difference between a dissolved substance and a gas is that the gas does not need the presence of the molecules of the solvent and their affinity to sustain it in the occupied space." This is almost word for word the statement of Gay-Lussac. The different colors of concentrated and diluted solutions of copper chloride were explained by Bizio as being due to a condensation or attenuation of the molecules, *i. e.*, a kind of dissociation. Of course this idea does not at all imply a dissociation of $CuCl_2$ into its ions Cu and 2Cl, as Bellati seems inclined to suppose. "The lack of precision in the mechanical conceptions of Bizio hindered their acceptance" says Bellati.

Another man who adhered to the idea of a close analogy between the gaseous and the dissolved states

was Rosenstiehl, who expressed his views in a note published in Paris in 1870. Rosenstiehl says that he has heard that Arago has been the first to compare the phenomenon of solution with that of evaporation but that he has not been able to find the quotation in which this view is expressed.—Probably Arago has been confused with Gay-Lussac.—Rosenstiehl drew the remarkable conclusion that "the osmotic force is analogous to the elastic force of vapors. Between the fluid column, which rises in an osmometer and the piston lifted by the elastic force of a vapor there is no other difference than that of the medium in which the work is effected."

In 1869 and 1873 Horstmann deduced from thermodynamics the laws of chemical equilibrium between gaseous substances. As he had already tested his theoretical results on known equilibria between gases, he next subjected an equilibrium between dissolved substances, namely the sulphates and carbonates of potassium and of barium in the presence of precipitates of the two barium salts, to the same formula as that which had proved valid for gases.

This equilibrium had been studied by Guldberg and Waage. In 1864 they had elaborated a theory of chemical mass-action according to which the "chemical force" with which two substances A and B in concentrations C_A and C_B, act upon each other is proportional to the product of these concentrations raised to certain powers, *i. e.*, to $C_A^a \,.\, C_B^b$. If then two new substances E and F were formed, as for instance in the interaction of two salts, and equilibrium was reached when the concentrations of those substances were C_E and C_F then

the chemical forces on both sides must be of the same magnitude, *i. e.*,

$$K \cdot C_A^a \cdot C_B^b = K_1 C_E^e \cdot C_F^f.$$

In 1867 they simplified this formula by assuming $a = b = e = f = 1$, so that the exponents were omitted. But on the other hand they introduced a complication by supposing that the chemical forces between A and B were not only dependent on their own concentrations but also on the concentrations of all other substances present in the solution. This complication was introduced in order to explain the influence observed in many cases of foreign substances on the equilibrium.

In order to test their ideas Guldberg and Waage carried out a great number of experiments both on the velocity of reaction on the solution of metals in acids (in which case the velocity was taken as a measure of the acting chemical force) and also on equilibria in which class that existing between K_2CO_3 and $BaSO_4$ on the one hand, and K_2SO_4 and $BaCO_3$ on the other was the principal example.

It was these experiments which Horstmann calculated by means of the formula which had proved valid for gases and he found them to be in good agreement with it. He concluded that the "disgregation" of a (dissolved) salt depends on the distance between its molecules, in the same manner as the corresponding property of a permanent gas, an assumption which also from other considerations seems to be probable.

In 1879 Guldberg and Waage again modified their theory and, citing Horstmann, they discarded from their equation the terms referring to the secondary action of foreign substances. In this way the analogy between

the gases and the dissolved substances in their chemical action was made perfect. They say that "these secondary actions may be neglected if the solutions are so highly diluted, that a further addition of solvent (water) gives rise to no sensible development of heat." Julius Thomsen, the renowned Danish thermochemist, was very well acquainted with the work of Guldberg and Waage and probably he was influenced by it when he concluded the first volume of his "Thermochemische Untersuchungen" (1882) with the following words: "The aqueous solutions of substances contain them in a condition which, just as the gaseous state, reveals their physical qualities in the simplest manner, so that a direct comparison of the two states is permissible." At that time the kinetic theory of heat was widely accepted by physicists and chemists. It was supported and had been worked out by such authorities as Clausius, Maxwell and Boltzmann. It was, in fact, regarded as absolute truth, almost like the two laws of thermodynamics. This whole subject was therefore often called "the mechanical theory of heat." Later on came a more sceptical time, when it was strongly maintained that thermodynamics may exist independently of the kinetic theory of heat and when it was regarded as a sign of progress to be able to discard all mechanical views regarding the nature of heat. Nowadays we have come back to the old view, and regard it as proved that the molecules possess a motion, the energy of which is proportional to the absolute temperature (cf. Lecture II).

Regarded from this point of view the sublimation of a solid substance such as camphor or iodine depends

upon the fact that some of its molecules possess such a violent motion that they can remove themselves from the sphere of attraction of the neighboring molecules. In the same manner the solution of a solid in a liquid must be explained as a consequence of molecular motion according to the mechanical theory of heat. This idea was expressed by Tilden and Shenstone (1883) "The solution of a solid in a liquid would accordingly be analogous to the sublimation of such a solid into a gas and proceeds from the intermixture of molecules detached from the solid, with those of the surrounding liquid. Such a process is promoted by rise of temperature, partly because the molecules of the still solid substance make longer excursions from their normal centre, partly because they are subjected to more violent encounter with the moving molecules of liquid." . . . "Such a theory however, serves to account only for the initial stage in the process of solution, and does not explain the selective power of solvents nor the limitation of solvent power of a given liquid."

Walden cites Mendelejeff as a precursor of the supporters of an analogy between gases and dissolved substances. Mendelejeff had stated (1884) that the densities of aqueous solutions containing 1 molecule of salts to every 100 molecules of water generally increase with the molecular weight of the salt. (There are some exceptions to this rule, *e. g.*, solutions of Li-salts are denser than equivalent solutions of NH_3-salts; compare "Valson's moduli," Lecture VI). "In extremely dilute solutions the dissolved substance exists in a dispersed or attenuated state similar to that in the gaseous state. Therefore we may hope, through the investigation of

the densities of solutions to find a method of determining molecular weights."

On closer inspection we find that the observed regularity does not tell us much more than that salt-solutions generally possess higher densities, the more concentrated they are. This depends upon the high specific weight of salts and especially of those with high molecular weights compared with water. If we extend the comparison to solutions of substances of a lower density than water, such as alcohol, the cause of the regularity is evident. We must therefore reject the claims raised in favor of Mendelejeff in this department.

As is seen from the quotations above, the great analogy between gases and dissolved substances was admitted by a great number of leading chemists. In order to give the required force to these opinions it was necessary to apply the laws of thermodynamics to them and this was done by van't Hoff. To understand the development of this side of chemical science we shall give a short review of the earliest work in this line.

As early as 1858 Kirchhoff had published some theoretical thermo-dynamical considerations on the vapor pressures of solutions, especially of sulphuric acid. In 1867, 1868 and especially in 1870, Guldberg worked out this important section of science in a most remarkable manner. He demonstrated that the lowering of the freezing point of a solution under that of the solvent as well as the corresponding increase of its boiling point is proportional to the corresponding lowering of its vapor tension and gave the constants which represent the factors of proportionality. He verified his theo-

retical deductions by means of the figures of Wüllner and of Rüdorff concerning the behavior of salt solutions in water. We now know quite well how important the similar deductions were later on in the hands of van't Hoff. Raoult (1878 and 1882) deduced these laws experimentally a little while afterwards and found the true law of depression of the vapor-pressure:

$$\log_e \frac{p - p_1}{p} = \frac{n}{N + n},$$

where p and p_1 are the vapor-pressures of pure solvent and of the solution in which n molecules of dissolved substance are mixed with N molecules of solvent. Guldberg also in 1870 deduced the law of change of solubility with temperature and pressure later deduced by van't Hoff. He even showed how the relative depression of the vapor-pressure changes with temperature.

Another great advance was made in 1869 in Horstmann's application of Carnot's theorem (or its special form, the formula of Clapeyron) to the evaporation and simultaneous dissociation of sal-ammonia, and he calculated its heat of evaporation from the observed vapor-pressure and found it to correspond very well with that experimentally determined by Marignac. The calculation was exactly similar to that by which the heat of evaporation of water is found from its vapor-pressure at different temperatures. A similar calculation was made by him in 1870 for the evolution of carbonic acid from carbonate of calcium according to Debray's experiments and for the dissociation of $Na_2HPO_4 + 12H_2O$ into $Na_2HPO_4 + 7H_2O$ and water vapor. In 1872 Guldberg made similar calculations for the dissociation pressure

of calcium carbonate and deduced the famous formula:

$$\frac{d \log p}{dt} = \frac{q}{ART^2} = \frac{Q}{2T^2}$$

where p is the dissociation pressure, T the absolute temperature, R the gas constant, A the inverse value (1/426) of the mechanical equivalent of heat, and q the heat of dissociation of 1 gram. This formula is simplified to the second form if Q is the heat of dissociation of 1 grammolecule, since then $AR = 2$ (better 1.985), as Guldberg had shown in 1870.

In 1873 Horstmann wrote his famous "Theorie der Dissociation" where he treats the general problem of dissociation of gaseous substances, and applies the results to the investigations of Würtz on amylene hydrobromide $C_5H_{11}Br$ and to those of Würtz and Cahours on pentachloride of phosphorus (PCl_5). Here he finds the great analogy between dilute solutions and gases. He quotes the figures of Thomsen regarding the "avidity" of sulphuric and nitric acid towards sodium hydrate and those of Guldberg and Waage on the reaction between barium sulphate and potassium carbonate at 100° which had served the latter when testing their law of mass action, a law which is also valid for the reactions of gases. In this way Horstmann was led to the conclusion regarding the analogy between dilute solutions and gases, cited above.

In 1878 appeared the far-reaching investigations of Willard Gibbs on the application of thermo-dynamics to chemical equilibria. In this work all conceivable problems in this field of science are treated theoretically.

But his important deductions were concealed in academical transactions, which were only very little known and therefore did not exert any sensible influence on scientific development. In 1882 Helmholtz independently wrote his well-known memoir on "free energy," containing general deductions very similar to those of Gibbs. In 1885 Le Chatelier published his interesting memoir, in which he, basing his theory on Wüllner's experiments, shows that the equation of Clapeyron may be used for calculating the change of the solubility of a substance with temperature.

The ground was therefore very well prepared from the theoretical side. But the last simple grasp of the problem failed, until van't Hoff in 1885 demonstrated the widely extended analogy between substances at high dilution and gases in their physical and chemical behavior. A year before this, he had published his important "Etudes de dynamique chimique," where he gave the formula found before by Guldberg for the change of the pressure of dissociation with temperature and showed that it also holds good for the change of the constant of a chemical equilibrium with temperature, if this constant replaces p and if Q represents the heat evolved in the reaction considered. A similar expression was used by Boltzmann in the same year for calculating the heats of dissociation of iodine and of N_2O_4. And also in the same year Le Chatelier had a little earlier than van't Hoff found the same general qualitative expression for the change of chemical equilibrium with temperature as is contained in van't Hoff's quantitative formula.

Van't Hoff's fundamental discovery in 1885 was

directly due to the investigations of De Vries and Pfeffer on the osmotic pressure of certain plant cells. They investigated a property well-known to cell-physiologists, namely that if cells are placed in aqueous solutions they take water from the solution, if this is weak, and give up water to it, if it is strong. With a certain concentration of the solution equilibrium is obtained. De Vries found that solutions of glycerol or of cane sugar, which contain the same number of molecules per liter, are in equilibrium with the same cells. Also equimolecular solutions of KCl, NaCl, KNO_3 and $NaNO_3$ are found to be in equilibrium with the same cells. But these salt solutions are only 0.6 times as concentrated as the corresponding solutions of glycerol or cane sugar which are in equilibrium with the same cells.

Now Moritz Traube in 1867 had given a method of preparing artificial cells, which possess the properties of attracting water from or of giving it up to surrrounding aqueous solutions according to their concentrations, just like natural cells. In 1877 Pfeffer used Traube's cells for measuring the force with which distilled water was attracted into such a cell filled with a solution of, *e. g.*, 1 per cent. cane sugar. If the solution in the cell is subjected to a certain pressure the water is driven out from the sugar solution: the sugar itself does not pass through the cell walls, which latter consisted of a thin membrane of ferro-cyanide of copper, precipitated in the porous walls of an earthenware vessel. At a certain pressure, which was found to be 505 millimeters of mercury at 6.8° C., equilibrium was reached so that no water went into the cell from the surrounding dis-

tilled water and no water was pressed out from the solution of cane sugar through the cell walls. This pressure, the so-called osmotic pressure of a solution of 1 per cent. cane-sugar, increases with temperature. It is nearly proportional to the concentration of the sugar-solution when this is changed.

These results of Pfeffer's measurements were communicated to van't Hoff by his friend De Vries, who asked for a theoretical explanation. Van't Hoff made the following simple calculation. A gas containing one gram molecule in 22,400 c.c. at 0° C. possesses a pressure of just 1 atmosphere or 760 millimeters of mercury. At 6.8° C. the pressure is a little higher, namely 779 millimeters, according to the law of Gay-Lussac. If this gas was expanded until it contained one molecule in 34,200 c.c., which is the concentration of a 1 per cent. solution of cane sugar—the molecular weight of cane sugar being 342—its pressure at 6.8° C. would according to Boyle's law be 508 millimeters. This figure agrees within 1 per cent. and within the errors of observation in Pfeffer's experiments with that, 505 mm., found for the osmotic pressure of an equi-molecular solution of cane sugar. In other words the osmotic pressure of this solution is equal to the pressure of a gas containing the same number of molecules in the same volume. Since further the osmotic pressure increases proportionally to the concentration (just as the gas pressure does according to Boyle's law) and within the errors of experiment as van't Hoff deduced from Pfeffer's figures, also to the absolute temperature (as in Gay-Lussac's law for gases), there exists a perfect analogy between the osmotic pressure of a solution (of cane sugar)

and the pressure of a gas containing the same number of molecules in the same volume.

As soon as this fundamental fact was stated, van't Hoff applied all the laws which had been deduced from thermodynamics for the pressures of gases and for saturated vapors, which correspond to saturated solutions, to the osmotic pressures of dissolved substances. Thus he found that he was able to deduce the general law of chemical equilibria (Guldberg and Waage's law); the law of the influence of pressure on chemical equilibria (Le Chatelier's law); the law of the temperature-variation of chemical equilibria; the law of partition of a substance between two different phases (law of Henry and law of Berthelot and Jungfleisch); the laws of vapor pressure and freezing point of solutions (laws of Raoult; the third law of Raoult regarding the boiling points was a little later deduced by Arrhenius, the connection between these laws having already been pointed out by Guldberg); the law of isotonic solutions (law of De Vries); the law governing the partition of a base between two acids according to the experiments of Jellet, Julius Thomsen and Ostwald; the law of the change of solubility with temperature, partially deduced before by Guldberg; the regularities found in the action of water on salts, according to experiments of Ditte; and the law with regard to the electromotive force of galvanic cells, concerning which Gibbs and Helmholtz had some years before (1878 and 1882) written fundamental works, in which they introduced the conception of "free energy."

The whole investigation of van't Hoff (1885) was

a triumphal march through the different domains of physical chemistry; only one difficulty, but a rather severe one, was found. The great majority of substances examined did not follow the law of Avogadro, as cane sugar did. This was already manifest from De Vries' investigations, according to which one molecule of sodium chloride exerts the same osmotic pressure as about 1.7 molecules of cane-sugar dissolved in the same quantity of water. To account for this difference, van't Hoff introduced a coefficient i (the isotonic coefficient) which was determined experimentally. This coefficient entered as an exponent into the formula for the chemical equilibrium, so that Guldberg and Waage's law was reduced to its first form (of 1864).

This was a great inconvenience, for it really spoilt the analogy between the dilute and the gaseous states of matter, but it was very soon eliminated by the theory of electrolytic dissociation. Therefore in the second edition (1887) of his fundamental memoir van't Hoff added the following remarkable words regarding the necessity of introducing the coefficient i: "Thus it seems rather adventurous to put Avogadro's law so strongly in the foreground, as I have done in this memoir" (in the memoir of 1885 very much less stress was laid on the validity of Avogadro's law for solutions) "and I would not have decided to do so, if Arrhenius had not, in a letter, pointed out the probability, that with salts and similar substances the question is really one of their division into ions."

A theoretical deduction of the law of van't Hoff regarding the analogy of the dilute and the gaseous

state of matter was given by Planck (1887) in order to explain the anomalies which led van't Hoff to introduce the coefficient i. He started from the hypothesis that for the energy U of a dilute solution containing n molecules of solvent and n_1, n_2, n_3, etc., molecules of dissolved substances the following expression is valid (at constant temperature):

$$U = nu + n_1u_1 + n_2u_2 + n_3u_3 + \ldots$$

where u, u_1, u_2, u_3, etc., may be regarded as the partial energies of one molecule of solvent or of dissolved substances, respectively, in very dilute solutions—so dilute that on further addition of solvent no heat is evolved. The same expression is valid for a mixture of gases in the same proportions. Therefore the gas-laws hold good for dissolved substances. The abnormal behavior of salts is due to a dissociation of their molecules.

The weakness of this deduction is evident; it might be that the expression quoted was true only for solutions so extremely dilute that they were not capable of being measured. Planck also conceded (1892) that by means of thermodynamics "nothing could be demonstrated regarding the qualities of the dissolved molecules, either in respect to their chemical or electrical properties, and that to this method could be ascribed no convincing conclusion, but only a heuristic signification."

Certainly the adherence of Planck and at the same time of Boltzmann, the two most prominent representatives of mathematical physics in Germany, helped in a

high degree to protect the new theory from the attacks of physicists. By their great authority they also gave a strong support to the new ideas in the eyes of chemists and of scientists in general, and this was of a value which should not be underestimated, especially during the first years of the growth and propagation of these ideas, which otherwise seemed revolutionary and therefore evoked a rather determined resistance.

LECTURE VI.

DEVELOPMENT OF THE THEORY OF ELECTROLYTIC DISSOCIATION.

THERE have been two different roads, which have led to views related to the modern theory of electrolytic dissociation, one empirical and one theoretical. The empirical one, inaugurated by Valson, is founded on the so-called additive properties of salt-solutions, the theoretical one, first entered upon by Gay-Lussac, Williamson and Clausius, is based upon considerations of the progress of chemical processes or the passage of electricity through salt solutions. Under salts are here included even acids and bases.

Valson measured the height to which salt-solutions rise in capillary tubes of glass. These heights are proportional to the capillary constant and inversely proportional to the density of the solution (provided of course that the internal diameter of the capillary tube remains the same). When he compared normal solutions, which contain equivalent weights of different salts in one liter of the solution, he stated that the capillary height might be conveniently calculated as the sum of three components, the one the capillary height of pure water and the other two corrections, which should be added, the one for the positive radical (now we say ion) of the salt and the other for its negative radical. These two corrections, which are generally negative, always remain the same for the same

radical independent of the other radical to which it is bound in the investigated salt. This is most clearly demonstrated in the so-called additive scheme, which shows that the difference of the investigated property (here capillary height) between a chloride and a nitrate is the same for the potassium salts as for the sodium or lithium or calcium salts, if the solutions possess the same number of equivalents per liter. The same is true of the difference between chlorides and sulphates, chlorides and carbonates and so forth. As an example we give the following differences in millimeters of the capillary heights for normal solutions. (The diameter of the glass tube was 0.5 mm., the temperature + 15° C.):

NH_4Cl 60.9, KCl 59.3, ½ $CdCl_2$ 56.5, LiCl 60.8, ½ $SrCl_2$ 58.0, ½ $BaCl_2$ 56.9, ½ $ZnCl_2$ 58.1, NaCl 59.6, H_2O 60.6.
Cl−Br: NH_4 2.2, K 2.2, ½ Cd 2.0, Mean 2.1.
Cl−I: Li 3.8, K 3.9, ½ Ba 3.8, ½ Zn 4.1, ½ Cd 4.0, Mean 3.9
Cl−SO_4/2: NH_4 1.2, K 1.1, Na 1.2, ½ Zn 1.1, ½ Cd 1.2, Mean 1.2.
Cl−NO_3: NH_4 1.1, K 0.9, ½ Sr 1.1, ½ Ba 1.0, Mean 1.0.

The capillary height of water was 60.6 mm., and was only exceeded by the capillary heights of normal solutions of NH_4Cl and LiCl, amongst the solutions examined. At the head are written the capillary heights of the chlorides from which the corresponding values of the other solutions may be calculated. The third line regarding Cl-Br indicates that the capillary height of a normal solution of NH_4Br is 60.9−2.2 = 58.7, of KBr 59.3 − 2.2 = 57.1 and of ½$CdBr_2$ 56.5 − 2.0 = 54.5.

The additive scheme demands that all the figures for Cl-Br should be equal and so forth. In reality this was found by Valson to correspond very nearly to his measurements.

Valson has drawn some conclusions from his measurements which I cite verbally because they have sometimes been misunderstood, which can well happen, as many technical terms were used in a different sense than now. He says: "Experience shows that the effects of capillarity are nearly proportional to the quantity (concentration) of the examined substance, but this is not true for concentrated solutions, in which the actions of the molecules are not independent of each other. It therefore seems that it is necessary that the saline molecules occur in a medium of sufficient volume, in order that they may be regarded as having reached the state of liberty. It is something analogous to the circumstances of the dissociation phenomena as stated by Mr. Henri Sainte-Claire-Deville, according to which the molecules of different substances do not manifest their specific properties and do not give their characteristic effects, if they are not brought to a suitable degree of attenuation (desagrégation)."

Here there is no question of a dissociation of the salt molecules, into their ions, or even of the additive properties, but only of the regularity that the difference of the capillary height of water and that of a dilute salt solution is proportional to its concentration, from which Valson concludes that the molecules are in an ideal state showing many regularities when they are diluted with a great quantity of water. This ideal state vanishes with higher concentrations, for which the said regularity is not observed. This opinion of Valson is still more emphasized in the following words: "If one combines the metals with different metalloidic radicles as for instance oxygen, chlorine, bromine, iodine, etc.,

one finds that the caloric equivalents of the binary compounds, referred to the dissolved state, exhibit constant differences amongst each other. One may explain this analogy in remarking that the capillary phenomena as well as the calorific ones, depend finally on the same property of the molecular movement, which generally is called *vis viva.*" This conclusion is rather confusing, the capillary phenomena really depend upon surface tension and are diminished when the molecular movement (vis viva) increases with temperature.

In reality the circumstance, that the additive scheme holds to a certain but rather low degree even for the heats of combination, reduced to the dissolved state, has been taken as an argument against the dissociation theory, and therefore we shall come back to this special case later on.

The capillary height is proportional to the capillary constant, which shows very small inequality for different normal solutions, and inversely proportional to the specific weight of the solution, which latter is subject to a rather great variation. Therefore the values of the capillary height show nearly the same regularities as the specific weights of normal solutions, or better, as the inverse value of this property, which is generally called the specific volume. It was therefore an advance when Valson a little later examined the specific weights of normal solutions and there found regularities similar to those for the capillary height. Later on Favre and Valson examined the changes of volume which occur on the solution of salts in water. On absolutely inadmissible grounds they calculated the heat which occurs on compressing one liter of water to 999 c.c. at 15° C.,

to be 7,576 cal., whereas in reality it is only 22.3 cal. (cf. p. 69 above). On the solution of one gram equivalent of a salt in water sometimes a contraction of 20 c.c. is observed, which on their supposition corresponded to about 150,000 cal., and arguing from this, they stated that an enormous change of the salt had taken place, which manifested itself as a "reciprocal independency" of the radicals of the salt "which it would be difficult to define now but which is very different from their original state." "The solution has the effect that it gives the elements of the dissolved substances an independency of each other." It may be remarked here that the solution of non-electrolytes, *e. g.*, of alcohol, in water, gives rise to similar great changes of volume.

Evidently this whole calculation and its consequences are absolutely erroneous. This becomes quite clear when we say that Favre and Valson would have found an infinite value for the calculated evolution of heat, if they had chosen the temperature at which water has its maximal density, and this value would have been $+\infty$ above and $-\infty$ below this temperature. The authors demonstrated by experiments that the different kinds of alums are to a great extent decomposed upon dilution into the two component sulphates, but that is something wholly different from the now pretended decomposition of, *e. g.*, NaCl into Na and Cl. We must therefore say that the ideas which have been developed by Favre and Valson are rather far remote from the theory of electrolytic dissociation.

On a closer investigation of the properties of salt solutions their additive character was shown in many

cases. Thus Kohlrausch found that the conductivity of a salt solution might be expressed as the sum of two conductivities, the one valid for the anion, the other for the cation of the salt. This rule of the "independent movement of the ions" held only within the same group of salts, *e. g.*, the salts composed of two monovalent ions such as KCl. Other values of the conductivity of the different ions were obtained for salts consisting of one bivalent and two monovalent ions such as K_2SO_4 or $BaCl_2$ and still others for salts composed of two bivalent ions such as $MgSO_4$. Gladstone and Bender observed similar regularities for the refractive index of solutions, Jahn for the magnetic rotation of the plane of polarization, G. Wiedemann for the molecular magnetism, Oudemans and Landolt for the natural rotatory power of the plane of polarization. The most evident example was the thermoneutrality of salts stated by Hess as early as 1840.

The most accurate measurements concerning the additive properties of salt solutions and just those properties which were at first considered by Valson, are due to Röntgen and Schneider.

For the relative compressibilities of 0.7 normal salt solutions (that of water = 1,000) they found the following values

	H	Diff.	NH_4	Diff.	Li	Diff.	K	Diff.	Na
I	—	—	954	14	940	8	932	8	924
NO_3	981	27	954	20	934	4	930	8	922
Br	981	28	953	19	934	4	930	7	923
Cl	974	29	945	17	928	9	919	2	917
OH	1,000	(8)	992	(97)	895	11	884	3	881
$\frac{1}{2}SO_4$	970	(117)	853	(40)	813	9	804	1	803
$\frac{1}{2}CO_3$	—	—	—	—	—	–	798	1	797
Mean		28		17		7		4	

The relative molecular volumes of 1.5 normal solutions were:

	NH_4	Diff.	K	Diff.	H	Diff.	Li	Diff.	Na
I	1,048	7	1,041	—	——	-	1,025	2	1,023
NO_3	1,043	11	1,032	14	1,018	2	1,016	−1	1,017
Br	1,038	13	1,025	14	1,011	0	1,011	1	1,010
Cl	1,028	12	1,016	14	1,002	1	1,001	0	1,001
OH	1,036	(52)	984	(−16)	1,000	(30)	970	0	970
$\frac{1}{2}SO_4$	1,066	—	——	—	1,027	(20)	1,007	—	——
$\frac{1}{2}CO_3$	——	—	1,012	—	——	—	——	—	984
Mean		10		14		1		1	

By molecular volume of the solution is here understood its volume compared with that of water containing the same total number of molecules at the same temperature; in the experiments it was 18° C. By normal solution is understood a solution containing one gram equivalent in 1000 grams of water.

The corresponding values for the constants of capillarity of 1.5 normal solutions were found to be:

	H	Diff.	NH_4	Diff.	Li	Diff.	K	Diff.	Na
I	——	——	113.14	− .09	113.23	−.36	113.58	−.26	113.84
NO_3	109.75	−4.11	113.86	− .36	114.22	+.30	113.92	−.33	114.25
Br	110.40	−3.93	114.33	− .10	114.43	−.25	114.68	−.05	114.73
Cl	110.88	−3.60	114.48	− .53	115.01	+.22	114.79	−.26	115.05
OH	111.45	(+5.36)	106.81	(−8.40)	115.21	−.33	115.54	−.33	115.87
$\frac{1}{2}SO_4$	112.49	(−3.42)	116.91	(− .70)	117.61	——	——	——	——
$\frac{1}{2}CO_3$	——	——	——	——	——	——	118.23	——	117.54
		−3.88		− .27		−.09		−.25	

These figures are very instructive. The additive scheme does not hold for all the solutions examined, as is seen from the figures put in brackets. It is necessary to take away some solutions, especially those indicated, namely, HOH, NH_4OH and $\frac{1}{2}H_2SO_4$, in order to find the regularities prevailing. These exceptions, which caused great difficulty for the pure empirical rule, will

be seen later on to give the best proof of the applicability of the dissociation theory.

It should be mentioned that Röntgen and Schneider emphasized the applicability of the rule of additivity with some marked exceptions—just those cited above—but did not feel justified to conclude that a dissociation of the salts into their ions takes place, notwithstanding that the corresponding theory was worked out partially before the authors published their work (1886).

In a memoir of 1885, in which Raoult gives the final results of all his measurements regarding the freezing points of salt solutions, he comes to the conclusion that this property is strongly additive in regard to the radicals of which the salt is composed. The molecular lowering of the freezing point might be calculated as a sum of the lowerings produced by the constituent radicals. For each negative monovalent radical, such as chlorine, bromine, hydroxyl, CH_3CO_2, NO_3, the lowering is 20; for bivalent negative radicals, such as SO_4, CrO_4, 11; for monovalent positive radicals such as H, K, Na, NH_4, 15; and for bi- or poly-valent electropositive radicals, such as Ba, Mg, Al_2, 8. Thus for instance the molecular lowering for nitric acid, $HNO_3 = 15 + 20$, *i. e.*, 35, it was observed to be 35.8; for aluminium chloride, Al_2Cl_6, it is calculated to be $8 + 6 \cdot 20 = 128$, found 129, etc.

Raoult cites some other investigations, indicating the additivity of different properties characteristic for salt solutions and then continues: "Then, the diminishing of the capillary heights, the increase of the densities, the contraction of the protoplast (the osmotic pressure investigated by De Vries), the lowering of the freezing

point, briefly *most of the physical effects produced by salts on the water dissolving them are the sum of effects produced separately by their constituent electropositive and electronegative radicals, which act as if they were simply mixed in the liquid.*

This fact, although it is no necessary consequence of the dualistic electrochemical theory of the salts, nevertheless confirms it in its principle. It indicates that the salts dissolved in water should be regarded as systems of particles, of which everyone is composed of solidary atoms and retains, unaffected by its state of combination (état de combinaison) with the others, a great part of its individuality, its action and its proper characters."

That there is in reality no question of a real dissociation (it is even said that the particles, *i. e.*, the ions are in a state of combination) is evident from the fact that, if this were the case, all the radicals ought to possess the same influence on the depression of the freezing point, whereas the action varies between 20 and 8. It is also clear from the utterance (*l. c.*, p. 406) that "the weak acids (such as HCN, CH_3CO_2H, $H_2C_2O_4$) always give an abnormal lowering of the freezing point which is about only half the normal value, as if the majority of their molecules were united two and two."

There is also a great number of other anomalies summed up in the following table:

Salt.		Molecular lowering Calculated.	Observed.	Ratio.
Cu, $(CH_3CO_2)_2$	8	+ 2·20 = 48	31.1	1.54
Pb, $(CH_3CO_2)_2$	8	+ 2·20 = 48	22.2	2.16
H, (CH_3CO_2)	15	+20 = 35	19.0	1.84
Al_2, $(CH_3CO_2)_6$	8	+ 6·20 = 128	84.0	1.52
Fe_2, $(CH_3CO_2)_6$	8	+ 6·20 = 128	58.1	2.20

Salt.	Molecular lowering Calculated.			Observed.	Ratio.
K, SbO, $C_4H_4O_6$	2·15	+ 11	= 41	18.4	2.23
Hg, Cl_2	8	+ 2·20	= 48	20.4	2.35
Pt, Cl_4	8	+ 4·20	= 88	29.0	3.04

Raoult tries to explain all those anomalies by supposing that double or triple molecules of these salts are formed in their solutions. The ratios given in the last columns indicate, according to Raoult's method of determination, the complexity of the supposed salt molecules. It varies between 1.52 and 3.04. In reality there is a great number of minor exceptions, which are not so very easy to determine, because the experimental errors in this older work of Raoult are rather great.

With Raoult's memoir of 1885 the arguments based upon the additive properties have reached their highest point. They did not lead to the hypothesis of a real dissociation, but only to the consequence "that the salts (*e. g.*, NH_4NO_3, Na_2SO_4) should be regarded as systems of particles (in these cases NH_4 and NO_3 or 2Na and SO_4 respectively) of which each is composed of solidary atoms (*i. e.*, atoms which are wholly bound to each other as, *e. g.*, N and 4H in NH_4, N and 3O in NO_3) and retains unaffected by its state of combination with the other (*e. g.*, SO_4 with the 2Na) a great part of its individuality." This is exactly the theory of radicals, according to which a molecule for instance of alcohol (C_2H_5OH) is composed of radicals, here C_2H_5 and OH, which "unaffected by their combination with each other retain a great part of their individuality." These arguments could never lead further, because of the many exceptions stated, which are, as we know now, due to a very low degree of dissociation. The non-conformity

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of these arguments to fact consists in supposing that the same degree of independency (dissociation) always occurs for the radicals, whereas in reality the degree of dissociation varies from very nearly zero (in weak acids such as HCN) up to nearly unity (strong acids and salts of monovalent ions in high dilution). As we know now, the exceptions, *e. g.*, water, ammonia, sulphuric acid, from the rule of additivity all possess a degree of dissociation which is notably different from unity, and the additivity holds strictly only for completely dissociated salts but practically for such as are dissociated to about 80 or 90 per cent.—the agreement with the rule being the greater the nearer the dissociation is to unity.

As I have said above, E. Wiedemann has adduced just one of the examples of additivity cited by Valson to show that the dissociation theory is false. He argued in the following manner: "If we replace chlorine by bromine in very dilute solutions of hydrochloric acid and of potassium chloride, the quantity of heat developed is the same in both cases." "Chlorine and bromine are certainly not dissociated at common temperature." The same is valid in the case of the displacement of chlorine by NO_3 or OH in dilute solution, in which case we have to calculate the heat of formation of, *e. g.*, KNO_3 and KOH respectively from their elements K, N and 3O or K, O and H and of its following solution in a great quantity of water. This is easily done by aid of the tables given by thermochemists. The results of such calculations were given by myself in the following table, giving the heat of replacement in great calories (1000 cal.) per gram equivalent.

	H	K	Na	Tl	½ Ca	½ Sr	½ Ba	Max. Diff.
$Cl-NO_3$:	−19.9	−13.9	−13.7	− 9.6	−16.4	−17.6	−15.7	10.3
NO_3-Br:	+33.5	+24.4	+25.5	+16.9	+30.9	+31.0	+28.1	16.6
Br–OH:	(−49.6)	− 8.1	− 6.1	−15.7	−37.0	−28.4	−22.5	30.9
OH–I:	(+64.1)	+23.1	+32.8	+26.8	+53.7	—	—	30.6

The figures regarding water are put in brackets because they are not valid for a very dilute aqueous solution (but for concentrated water) and therefore do not agree with the conditions demanded by Valson and Wiedemann.

Compare this table with the following one of the corresponding heats of neutralization of strong bases with strong acids in dilute solution, adduced by myself in favor of the dissociation theory:

	KOH	NaOH	LiOH	KOH
HCl, HBr or HI	13.75	13.75	13.9	13.8
HNO_3	13.8	13.7	——	13.7

	½ CaO_2H_2	½ SrO_2H_2	½ BaO_2H_2	Max. Diff.
HCl, HBr or HI	14.0	14.1	13.85	0.35
HNO_3	13.9	13.9	13.9 (14.15)	0.2 (0.45)

The figures for HCl, HBr and HI are as Berthelot has tabulated them. For ½$Ba(OH)_2$ Berthelot gives 13.9, Thomsen 14.15—without doubt the figure of Berthelot is the probable one. All the figures are valid for common room temperature (18° C.). The values given in the last column are the differences between the smallest and the greatest figure in every horizontal line. This maximal difference ought to be zero or fall within the magnitude of experimental errors if perfect additivity prevailed, as is really the case for the heat of neutralization, but not at all for the heat of displacement, which therefore has been wrongly

cited by Valson and by E. Wiedemann as a (nearly) additive property.

The theory proposed by Gay-Lussac regarding the "equipollency" of salts in solution is the first one (1839) that reminds us of the theory of electrolytic dissociation. In 1850 Williamson gave a theoretical explanation of the fact that in the formation of ethyl ether $C_2H_5OC_2H_5$ in the presence of sulphuric acid, H_2SO_4, this latter is not consumed by the chemical process, which therefore is a catalytic one according to the terminology proposed by Berzelius. Williamson expressed the opinion that in the first stage $C_2H_5.OH$ and $H_2.SO_4$ exchange radicals through double decomposition so that HOH and $C_2H_5.H.SO_4$ are formed. After this process a second one takes place in which $C_2H_5.H.SO_4$ and $C_2H_5O.H$ change radicals through double decomposition so that ethyl ether $C_2H_5O.C_2H_5$ and sulphuric acid $H.H.SO_4$ are formed. The total change due to the two processes is therefore a formation of ethyl ether $C_2H_5.O.C_2H_5$ and water H.O.H from two molecules of alcohol $C_2H_5.O.H$. The quantity of sulphuric acid is unchanged, it serves only to bind the water formed during the process. It should be observed that C_2H_5OH in the first process is decomposed into C_2H_5 and OH, in the second one into C_2H_5O and H. This corresponds to fact.

Williamson generalized this idea and said that in a solution there is a perpetual change of radicals between the molecules. In this way the fact was explained that, in mixing two salts consisting of different radicals, all the four possible salts were rapidly formed as Gay-Lussac maintained (cf. p. 75 above). The same must also be true regarding molecules of similar composition.

Thus for instance in a solution of hydrochloric acid, H.Cl, an atom H does not always remain bound to the same atom of chlorine but exchanges it for new atoms of chlorine, the one after the other. He gives still another example: if we mix a solution of Ag_2SO_4 with one containing HCl, then some few molecules of H_2SO_4 and AgCl are immediately formed. The AgCl-molecules are very slightly soluble and precipitate so that HCl and Ag_2SO_4 are not formed again. But new molecules of H_2SO_4 and AgCl appear in the solution and the newly formed AgCl precipitates again. The process goes on in only one direction until there remains only such a small quantity of AgCl that the solution is just saturated in regard to it. This coincides wholly with the theory on "equipollency" of salts in solution proposed by Gay-Lussac in 1839.

It is not by chance that Williamson has chosen the electrolytes (salts, acids and bases) as example of his principle. For in the electrolytic solutions these changes of radicals—we now say ions—go on instantaneously as in the example above. All attempts to measure the velocity of reaction in cases, when electrolytes exchange their ions, have been in vain on account of their extreme rapidity. On the other hand similar reactions, in which non-electrolytes (or perhaps better stated extremely weak electrolytes) play a part, generally proceed slowly, as we shall also see later in regarding the processes characteristic of the formation of ethyl ether.

According to the law of Faraday each monovalent ion carries a charge of about $4.5.10^{-10}$ electrostatic units, the positive ions as H, NH_4, K and generally metals, of

positive, the negative ions such as Cl, CN, NO_3, ClO_3, etc., or generally negative radicals, of negative electricity. What will now happen if we place a solution containing an electrolyte in a vessel between two electrodes of different potential? The surface of the fluid will instantaneously assume a charge, so that positive ions are driven against the negative electrode and negative ions against the positive one. The different molecules will therefore be turned around until they stand with the chlorine ion to the left as in the molecules in the figure representing this case (Fig. 2, line 2). Or at least a majority of the HCl molecules will turn their chlorine to the left, their hydrogen to the right. In the exchange of ions between the HCl molecules, a majority

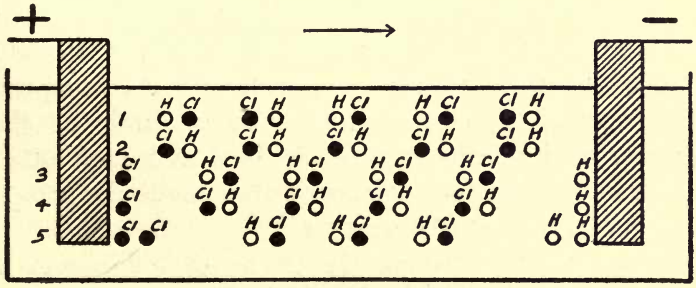

FIG. 2. Grotthuss' chain.

of the chlorine ions will wander to the left, the majority of the hydrogen ions to the right. Then they carry their charges with them and the said movement of the ions corresponds to a transporting of positive electricity in the direction of the arrow from left to right. Negative electricity wanders from the right to the left, which is equivalent to a wandering of positive electricity in the opposite direction. This is about the position taken by Grotthuss as early as 1825 and represented by Fig. 2.

It is just this latter idea which has been developed by Clausius in a memoir of 1857 without a knowledge of Gay-Lussac's or Williamson's paper. Clausius tried to explain how the law of Ohm may hold for electrolytic solutions, which had been proved by experiment. Ohm's law demands that even the least electric force causes a motion of the ions. Hence if these were bound to each other in the electrolytic molecule, so that a certain force were necessary to tear them asunder, as was and is generally believed amongst chemists, just this minimum of electric force (slope of potential) would be necessary for establishing an electric current; this is in contradiction to Ohm's law. Clausius drew the conclusion that the ions in electrolytic molecules are not fixed to each other, but might be exchanged for ions from other molecules just as Williamson had supposed. "The frequency of such mutual decomposition depends upon two circumstances, firstly on the greater or less coherence of the ions with each other and secondly on the violency of the molecular movement, *i. e.*, on the temperature."

Clausius also considers the theory of Williamson to which a chemist had directed his attention and says that "Williamson speaks of a perpetual change of the hydrogen atoms (between the HCl molecules), whereas for the explanation of the conduction of electricity it suffices that at the collisions of the molecules now and then, and perhaps relatively seldom, an exchange of the partial molecules (*i. e.*, ions) takes place."

"The increase of conductivity with temperature is explained in an unconstrained way by this theory," Clausius says, "because the greater violence of the

molecular movement must contribute to an increased reciprocal decomposition of the molecules."

Of course it must be regarded as very much strengthening the hypothesis of mutual exchange that three leading scientists, of whom two were chemists and the third a physicist, from apparently quite different empirical premises have been led to the same conclusion, and therefore it seems just to attach the names of all three of them to their hypothesis. The form given to it by Gay-Lussac and Williamson corresponds better to our present knowledge. A "perpetual exchange" comes much nearer to real dissociation than an "exchange now and then." Further, there have been objections against Clausius that according to his theory the conductivity should be proportional to the number of collisions of electrolytic molecules, *i. e.*, to the square of their concentration, whereas it really increases more slowly than in proportion to this quantity. Also the explanation of the increase of conductivity with temperature, given by Clausius, has not proved successful. In most cases the degree of dissociation decreases a little with increasing temperature, and the increased conductivity depends upon the diminishing of the internal friction with temperature.

The renowned Italian physicist Bartoli has expressed a similar theory, where dissociation is spoken of directly, in the year 1882. He investigated the so-called residual current, which is observed to pass through an electrolyte, even if the electromotive force necessary for its decomposition is not reached. Bartoli gives two different theories for the explanation of the residual current. Either the polarization, which hinders elec-

trolysis, disappears slowly by means of diffusion of the polarizing substances from the electrodes, or there is a dissociation of the electrolytic molecules. The first theory is generally accepted as the right one and was already at that time after Helmholtz's and Witkowski's important investigations (1880). The second one further demands that the degree of dissociation is proportional to the third power of the acting electromotive force, that is, if no electromotive force acts, it is zero (to the third power), and this case is just the one for which the modern dissociation theory demands a high degree of dissociation, which is further independent of the acting electromotive force, if there is such a one. The claims of priority raised by Bartoli in 1892 regarding the theory of electrolytic dissociation can therefore not seriously be discussed. It ought well be said that it would have been much more adequate if he, like his predecessors, from Gay-Lussac to Valson had, refrained from drawing such a wide-reaching conclusion, as that salts are dissociated, from such a small number of facts.

In 1883 I investigated the conductivity of electrolytes as depending on their concentration and temperature and came to the conclusion (published 1884) that their solutions contain two different kinds of molecules, of which the one is a non-conductor, the other conducting electricity in consequence of properties attributed to it by the hypothesis of Gay-Lussac, Williamson and Clausius. These latter were simply called active molecules. The number of active molecules increases with dilution at the expense of the inactive ones and tends to a limit, which is probably first reached when all inactive molecules have been transformed into active

ones. At very high dilutions the additive property of the conductivity postulated by Kohlrausch is not only true within certain groups of electrolytes of similar composition but for all electrolytes of whatsoever composition. An acid is the stronger the greater its conductivity is. At infinite dilution all acids have the same strength. These assertions were demonstrated to be in accord with the thermochemical measurements of Berthelot and Thomsen. Similar rules are valid for bases. Chemical activity therefore coincides with electrical activity. Water, alcohols, phenols, aldehydes, etc., which exchange ions with electrolytes are also electrolytes. The relative conductivity of water increases more rapidly with temperature than that of acids, bases or salts. Therefore the hydrolysis of salts increases with temperature. The results of Thomsen's, Guldberg's and Waage's, and especially of Ostwald's measurements of chemical equilibria were discussed and their discrepancies with Guldberg and Waage's law explained as dependent on the lowering of the activity of the examined weak acids caused by the presence of their salts and of strong acids. The heat evolved in the neutralization of a wholly active acid with a wholly active base is always the same and equal to the heat which is consumed in the activation of an equivalent quantity of water. The deviation of the heat of neutralization of weak acids or weak bases from the said value is due to the heat necessary for their activation.

In a reaction of ferrocyanide of potassium $K_4.C_6N_6Fe$, the ions of which are 4K and the rest, with other electrolytes, ferrocyanides and potassium-salts are always formed but not ferrous or ferric salts, because there

occurs only a rearrangement of the ions. Therefore the ion contained in the ferrocyanides cannot be detected by means of ordinary reagents on iron, which are all electrolytes.

When this memoir was written (1883) the measurements of Raoult on the freezing point of salt solutions had not appeared. Therefore it was regarded as too bold to state verbally that the active molecules were dissociated into their ions and it was only maintained that they should be subject to the conditions demanded by the hypothesis of equipollency. Soon afterwards Raoult's aforementioned measurements were published and their theory given by van't Hoff (1885). Immediately after that I calculated the coefficient of activity from the conductivity figures and the degree of dissociation which was necessary to explain the values i of van't Hoff, calculated from Raoult's data. A very good agreement was found and then the basis for an open declaration of the state of dissociation of electrolytes was found strong enough (1887). The word activity was replaced by the word electrolytic dissociation.

Immediately after my memoir of 1884 had appeared, Ostwald carried out a great number of measurements, showing that the velocity of reaction, when different acids exert a catalytic action, is, as my theory demanded, nearly proportional to their conductivity, and further that the relative strength of weak acids increases with dilution. In 1889 I showed that the catalytic action of different acids on inverting cane sugar, if it is corrected for the so-called salt-action, is proportional to the concentration of the hydrogen-ions present.

Ostwald, Planck and van't Hoff and Reicher simultaneously and independently of each other applied the law of mass-action on the equilibrium between ions and undissociated molecules of an electrolyte (1888). Ostwald found that this law really holds good for weak acids. Van't Hoff and Reicher were not content with the figures already published regarding the conductivity of weak acids and therefore they performed extremely accurate redeterminations, which gave an excellent agreement with the demands of the said law, which was called for this special case Ostwald's law. Planck finally did not succeed with the application of this law to salts, and this disagreement for strongly dissociated electrolytes still persists. Later on (1894) Bredig proved that Ostwald's law is valid also for weak bases.

From the law of van't Hoff regarding the change of chemical equilibria with temperature (cf. p. 83 and 84) I calculated the heat of electrolytic dissociation of different weak acids and showed it to be in perfect agreement with the observed heats of neutralization. Kohlrausch and Heydweiller did the same work for the most important and most difficultly determined of all examined electrolytes, namely water. In two new memoirs I determined the general laws of equilibrium between electrolytes. Ostwald demonstrated the extreme usefulness of the new theory for general and analytical chemistry. (1900 and 1904.)

The chief points of the theory of electrolytic dissociation were then fixed.

LECTURE VII.

VELOCITY OF REACTION.

THE first velocity of reaction studied was that on the inversion of cane-sugar investigated by Wilhelmy, in the year 1850. This process has a great practical use, as the determination of the quantity of cane sugar in a solution depends upon it. Wilhelmy used the saccharimeter of Soleil, the same instrument which was in use in the sugar-factories. It was known that the hydrolysis (decomposition with addition of water) of cane sugar may be carried out at low temperatures if an acid was added to the sugar solution. It was the velocity of this latter reaction, which was a typical example of what Berzelius called catalytic processes, that was the object of Wilhelmy's investigation. He stated that temperature exerts a great influence, he therefore tried to carry out his experiments at a not too variable temperature by placing his vessels containing the solutions of cane-sugar in a large vessel of water, heated by a spirit flame of constant size, or at lower temperature in a very large heat-isolated vessel filled with water.

Wilhelmy found that the general law, which holds for the fall of temperature to that of the surrounding temperature (Newton) or for the loss of electricity from a charged conductor (Coulomb), is also true for the transformation of cane sugar, namely that the transformed quantity in a given short time is proportional to the

remaining quantity. The strong acids: sulphuric, hydrochloric, nitric and phosphoric were found to be effective, but acetic acid had no appreciable influence (in fact it gives the same effect as the strong acids, but after a much longer time).

As an example we cite some experiments with nitric acid at 15° C.

Time of Reaction (Min.).	$A-x$ Quant. Sugar.	$\log \frac{A}{A-x}$.	$K=\frac{1}{t}\log \frac{A}{A-x}$.
0	65.45	———	———
45	56.95	0.0605	0.00134
90	49.45	0.1217	0.00135
150	40.70	0.1981	0.00132
210	33.70	0.2880	0.00137
270	26.95	0.3851	0.00142

The time law proposed by Wilhelmy leads to the expression

$$\log A - \log (A - x) = Kt,$$

where t is the time of reaction, x the quantity of transformed sugar after that time, A the quantity of sugar present at the beginning and K a constant. The formula expresses very well the progress of the process; it has been confirmed later by a great number of investigators.

It is possible to invert the cane sugar without the addition of acids at higher temperatures, *e. g.*, in autoclaves above 100° C. Of course this process goes on also at low temperatures but so slowly that it cannot conveniently be measured. The same process is also promoted by an enzyme called invertase, which is produced by yeast cells. It was believed for a long time, according to experiments performed by V. Henri, that this process obeys another time law than that relating to inversion by means of acids. Hudson has shown

that the exceptional behavior, found by Henri, depends upon the abnormal rotatory power (the so-called mutarotation) of the components of invert sugar, when they are recently formed. The values of x, *i. e.*, the transformed quantity of sugar, were therefore, in Henri's determinations, affected by great errors. It is possible to avoid this error by adding a trace of alkali to the solution of invert sugar, which very rapidly reaches its end value of rotating power under such circumstances. When these measures are taken, the change of cane sugar by means of invertase goes on according to the same law as if it were promoted by acids. This observation is very important as it shows again that the supposed difference in action of organic products (enzymes) and inorganic substances (acids) is not a real one. It is to be hoped that the corresponding irregularity found by Henri, his pupils, and others in the transformation of other sugars, will also disappear on closer investigation. This has already been proved by A. E. Taylor regarding the hydrolysis of maltose by means of maltase and that of starch with salivary amylase. That the inversion caused by means of acids goes on regularly depends upon the destruction of mutarotation by acids, which is not quite so rapid as that of alkalies, but still sufficient to prevent serious disturbances.

The said hydrolysis is also caused by ultra-violet light. Most reactions, especially hydrolytic ones, possess the same peculiarity as the inversion of cane-sugar in that they are catalyzed by hydrogen or hydroxyl ions (*i. e.*, by the presence of acids or bases) and by special enzymes. High temperature or ultraviolet light act

in the same manner. In the yeast cells there is another enzyme, zymase, which carries the process further when cane-sugar has been transformed to glucose. Zymase transforms it to alcohol and carbonic acid; probably lactic acid is an intermediary stage. On the other hand Duclaux showed that glucose in the presence of potassium hydrate or ammonia (*i. e.* hydroxyl ions) in sunlight gives alcohol and CO_2. If $Ba(OH)_2$ was used as the alkali the process went on only as far as the formation of lactic acid, which by the means of potassium hydrate and sunlight could further on change to alcohol and CO_2. Buchner and Meisenheimer found that sunlight is not absolutely necessary. They boiled inverted cane-sugar with strong KOH and thus produced alcohol without sunlight. Nencki and Sieber stated that glucose with 0.3 per cent. KOH gives lactic acid after 10 days at 35–40° C. Hanriot continued this process by boiling calcium lactate with calcium hydrate and obtained alcohol, just as Duclaux by means of sunlight.

We have here a number of reactions, namely:

1) $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$ (catalyzer
cane sugar water glucose lævulose
H-ions or invertase or light).

2) $C_6H_{12}O_6 = 2CH_3CHOHCOOH$ (catalyzer OH-ions
glucose lactic acid
or light or yeast).

3) $C_3H_6O_3 = C_2H_5OH + CO_2$ (catalyzer OH-ions or
lactic acid alcohol carbonic acid
light).

Evidently in Duclaux's experiments with $Ba(OH)_2$

the process was brought to a relative standstill because of the slight solubility of the barium lactate, when this intermediary product had been formed.

Other hydrolytic processes of very high importance, which are accelerated by hydroxyl or hydrogen ions and by special enzymes, namely trypsin and pepsin, are the so called digestive processes. The most important natural process, namely the formation of sugar from carbonic acid and water by the means of the catalytic action of the chlorophyll in the green parts of plants, probably takes place through a previous formation of formaldehyde, HCOH, and oxygen (O_2) from CO_2 and H_2O. It has recently been found possible to reproduce this photochemical process without the help of living organisms (D. Berthelot, Stoklasa).

In many cases the process itself produces a substance which accelerates it. Thus for instance if we dissolve copper in nitric acid, nitrous acid i formed, which accelerates the solution. Therefore if we put pieces of copper in, say 10 per cent., pure nitric acid, the copper is at first very slowly attacked; but the velocity of reaction increases so that after a time the reaction is violent, giving rise to a strong current of gas-bubbles. Such a process is the inversion of cane-sugar without acids at high temperatures. The cane sugar itself has a weak acid reaction, but its hydrolytic products, glucose and still more laevulose have much stronger acid properties as Madsen found. Therefore the reaction goes on with accelerated velocity, until finally very little cane-sugar is left, so that the process becomes complete by degrees. Such an "autocatalytic" process is also the saponification of an ester, *e. g.*, ethyl acetate by means

of water. At first the hydroxyl ions of the water produce saponification just as bases. The product, acetic acid, diminishes the quantity of the hydroxyl ions, so that the process goes on more slowly. But the hydrogen ions of the acetic also cause a saponification although they are not so active as the hydroxyl ions (they act 140 times less), and when they have increased to a sufficient number the process is accelerated after it has passed through a minimum, when the hydrogen-ions are 140 times as many as the hydroxyl-ions. This reaction has been studied by Wijs, who found that the experiment wholly confirmed the theory.

Even the common growth of organisms, *e. g.*, bacteria, has been regarded as such an autocatalytic process. If bacilli, *e. g.*, coli bacilli, are inoculated into a solution, containing their nourishment with a certain quantity of oxygen over it, and the whole is shaken so that oxygen is continuously carried to the bacilli, these are first increased in number, each independent of the others, so that the number of bacilli increases according to an exponential function, which as the curve shows is suddenly broken down, when the oxygen or nourishment begins to be nearly consumed. This phenomenon has been studied in my laboratory by Mr. Thor Carlson.

The growth of a single organism shows similar peculiarities. To begin with the increase, measured by weight, becomes greater and greater, then it is nearly constant, and thereafter decreases.

A very important case of reactions which are hampered by their own reaction products has been studied by me. If ammonia acts upon ethyl acetate, which is supposed to be present in great excess so that its quan-

tity may be regarded as constant, then the velocity of reaction is proportional to the number of hydroxyl ions present. The progress of the reaction is followed by means of the conductivity of the ammonium acetate formed. Now the number of hydroxyl ions is almost inversely proportional to the quantity of ammonium acetate already formed and therefore the velocity of reaction is also inversely proportional to the said quantity. This leads to the differential equation

$$\frac{dx}{dt} = \frac{K(A-x)}{x} \cdot P,$$

where A is the quantity of ammonia present from the beginning, x the quantity of ammonium acetate formed, K a constant and P the quantity of ethyl acetate which may also be regarded as a constant. When x is small compared with A we obtain:

$$xdx = KAPdt$$

or integrated:

$$x^2 = 2KA \,.\, P \,.\, t.$$

This formula tells us that the reaction proceeds so that the quantity of ammonium acetate is proportional to the square root of the time and also of the quantities of ethyl acetate (substrate) and reagent (ammonia). The truth of this premise is seen from the following figures, found for 0.66 n. ethyl acetate at 14.8° C.

t	x obs.	x calc.	$17.3\sqrt{t}$	t	x obs.	x calc.	$17.3\sqrt{t}$
1	17.5	19.4	17.3	10	51.2	51.3	54.7
2	25.5	25.2	24.5	15	59.6	59.7	67.0
3	30.7	30.6	29.9	22	67.5	68.6	81.1
4	34.7	34.9	34.6	30	74.5	74.7	94.7
6	41.5	41.7	42.4	40	80.7	80.7	109.4
8	47.0	46.9	48.9	60	88.2	88.2	134.0

The time t is given in minutes, x in per cent. The column $17.3\sqrt{t}$ agrees well with x obs., until this exceeds 50 p. c. After that the x calculated found according to the exact integral of the last differential equation holds good.

The said rule that the transformed quantity is proportional to the square root of the acting quantity and time is called Schütz's rule and holds for a great number of reactions in physiological chemistry, amongst others digestion by means of pepsin or of trypsin, the hydrolytic action of lipases on fats, etc. As an instance some figures given by Schütz may serve for the quantity formed in the action of different quantities of pepsin at 37.5° C. on the same quantity of egg-albumen, freed from globulin.

Quantity of Pepsin P.	1	4	9	16	25	36	49	64
Quantity of peptone found	9.4	20.6	32.3	45.4	55.2	65.0	76.0	85.3
$10.8\sqrt{P}$	10.8	21.6	32.4	43.2	54.1	64.9	75.7	86.5

Experiments regarding the influence of time are given by Sjöqvist for peptic digestion, by Stade for the lipolytic action of gastric juice and by others. The agreement with the exact formula is in most cases very satisfactory.

In this case the expression Pt enters into the final formula. Therefore the same quantity of reaction-product is produced by the enzyme quantity q in 1 hour as by the quantity 1 acting during q hours on the same quantity of substance. In many investigations of a physiological-chemical nature, it is easy to determine a certain point of decomposition, *e. g.*, when milk coagulates, when peptization, *i. e.*, liquefaction of gels

is reached, etc. In such cases it is generally stated that the necessary time is inversely proportional to the quantity of enzyme adapted to the experiment.

I have laid so very great stress upon the fact that we may find Schütz's rule to hold good for simple inorganic processes, also because at an earlier stage it was maintained that this rule was peculiar to the action of ferments in contradistinction to catalyzers, which are not prepared by living organisms. The deduction of this rule indicates that it is applicable, as soon as one of the reaction products reacts with the catalyzer, so that the free quantity of this substance is nearly inversely proportional to the quantity of reaction products. The deduction has also given a formula which holds for any magnitude of the transformed quantities whereas the rule of Schütz is not reliable for higher values of x than about 50 per cent.

As we have seen before, Williamson explained the peculiar action of catalyzers by stating that they give intermediary products of reaction from which the catalyzer is formed again in a later chemical reaction. Thus for instance, according to Williamson, the sulphuric acid in the formation of ethyl ether from alcohol at first gives ethyl sulphuric acid $C_2H_5HSO_4$, which thereafter reacts with alcohol to give back sulphuric acid and form ether. The two steps of this reaction are the following:

1) $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$,

2) $C_2H_5HSO_4 + C_2H_5OH = C_2H_5OC_2H_5 + H_2SO_4$,

or taken together:

$$2C_2H_5OH = C_2H_5OC_2H_5 + H_2O.$$

In reality the process is a dehydration of the alcohol and depends upon the binding of H_2O to the sulphuric acid. Therefore the process is very much retarded when a considerable quantity of water has been formed.

This process has been investigated by Kremann. He found that reaction 1 goes on rather rapidly at moderate temperatures and in the absence of water, the constant of reaction being 0.00112 at 40° and 0.0044 at 51°, corresponding to an increase in the proportion 1 to 3.63 in an interval of 10° C. The velocity constant of the formation of $C_2H_5HSO_4$ is about 1.7 times greater than that of its decomposition. In aqueous solution the velocity constants are about 50 times less (investigated for the decomposition of $C_2H_5HSO_4$) and their increase in an interval of 10° C. about as 1 to 1.99. Hence we conclude that the reaction is hampered in a high degree by the presence of water and that in the higher degree the lower the temperature is. Reaction 2 is inappreciable at low temperatures and can only be investigated above 100° C. Its velocity sinks very rapidly with the increase of the water formed. Its rate of increase with temperature is in about the proportion of 1 to 2.35 in an interval of 10° C. at 117.5°.

The velocity of the total reaction is determined by the slow one, *i. e.*, the second one, of the two partial reactions. In any case Kremann has shown that Williamson's theory of the formation of ether is correct.

The said process is a very complicated one. There are some other compound processes, which show a greater regularity. Amongst those the radioactive changes, which are independent of temperature and concentration, have been very closely studied, especi-

ally by Rutherford. In some cases, as with the radioactive deposit from actinium emanation, the velocity of reaction characteristic of the two consecutive processes are very different from each other, the actinium A being decomposed to 50 per cent. in 35.7 minutes, whereas the corrresponding time for actinium B is 2.15 minutes. Then the total process except at the very beginning may be regarded as a reaction going on with the velocity of the first reaction. In other cases as with the decay of the excited activity from radium emanation there are products, radium A, radium B, and radium C, which do not differ so very much from each other in their rate of decay, the corresponding times being 3, 21 and 28 minutes respectively. In this case the total decay, measured by means of the emitted (β or) γ rays, which accompany the decomposition of radium C, gives totally different time curves, according to the time during which the radioactive deposit has been formed. Through a thorough examination of the different possible cases, the different processes have been separated from each other and the rate of decay for each of them determined.

Probably the effect of catalyzers depends in most cases, just as in the case of the formation of ether, on their entering into intermediary chemical reactions from which they are regenerated in later reactions. In some cases as with platinum sponge, or with catalyzers in suspension the effect is probably due to an adsorption of the reagents on the catalytic agent.

It is well known that van't Hoff introduced the notion monomolecular, bimolecular, etc., reactions according to the number of molecules which, represented by the

chemical equation react upon each other, and for each of them a certain equation of reaction is characteristic. In many cases, especially when the number of the reacting molecules is great, the experimental results agree better with an equation of reaction corresponding to a lesser number of reacting molecules than is expressed be the chemical equation. In such cases an explanation of the seemingly abnormal behavior of the reaction has been found by the supposition that the investigated reaction is composed of two or more partial reactions of which the slowest one corresponds to the equation found experimentally. The hypothesis made has in some cases been verified experimentally.

As has been known from the times of the alchemists, temperature has a very great influence in hastening chemical processes. This was also stated by Wilhelmy, when he investigated the inversion of cane sugar. He found that the velocity of reaction increases nearly exponentially with temperature. The same was stated by Berthelot for the formation of ester from an alcohol and an acid, a reaction which, being one of the first examined rather closely, has played a preponderating rôle in this chapter. The formula, representing the velocity k of reaction is then:

$$\frac{d \log k}{dt} = B; \; k_t = k_0 \, 10^{Bt}.$$

Berthelot has himself said that the experiments were not sufficient in number for ascertaining if his formula is correct. The values given by him are

Temp.	k (obs.)	k (calc.)	B
8°	0.0004	0.0004	—
85°	0.074	0.0456	0.0281
100°	0.17	0.115	0.0307
170°	8.50	8.50	0.0243

The value of B decreases with rising temperature and this is the case for most processes studied hitherto. I therefore in 1889 examined the different determinations available at that time and found that another formula gives good results, viz.:

$$\frac{d \log k}{dt} = \frac{A}{T^2}; \log k_1 = A \frac{T_1 - T_0}{T_1 T_0} + \log k_0$$

where A is a constant and T designates absolute temperature. This formula, as well as that of Berthelot, is a special case of one proposed by van't Hoff and containing both the two terms occurring in the two formulas above.

$$\frac{d \log k}{dt} = \frac{A}{T^2} + B.$$

I found that the formula with only A/T^2 corresponds very well and in most cases better with the experimental results of different investigators than the empirical formulæ proposed by these investigators do. It has a theoretical meaning and must be preferred to formulæ containing a greater number of empirical constants, as does the formula of van't Hoff.

Van't Hoff called attention to a rather remarkable circumstance, namely that the increase in the value of k for 10 degrees is in most cases about in the proportion 1 to 2 or 1 to 3. But there are rather great exceptions; thus the decomposition of phosphoreted hydrogen PH_3 into its elements accelerates very much more slowly with temperature, namely in the proportion 1 to 1.2 for an interval of 10 degrees. But it must here be remarked that the observations are made (by Kooy) at 256 and 367° respectively, so that if my formula

is accepted the quotient increases to 2.5 at 27° C. The same remark may be made regarding the gas reaction studied by Smits and Wolff:

$$2CO = CO_2 + C,$$

which according to the chemical equation ought to be bimolecular, as 2 molecules of CO are necessary for the reaction, but which is found to be monomolecular. This is explained by assuming two consecutive reactions of which the first has a much smaller velocity than the second, namely:

$$1)\ CO = C + O,$$

$$2)\ CO + O = CO_2.$$

The velocity of this reaction is found to increase in the proportion 1 to 1.42 for 10° between 256° and 340. Reduced to 300° abs. (=27° C.) the increase reaches 1 to 3.53 for 10° C. The extreme values of the said proportion amongst the processes cited by van't Hoff seem to be shown by the two reactions which have been studied more than any other, namely the inversion of cane sugar and the saponification of ethyl acetate by hydroxyl ions with the values 1 to 4.0 and 1 to 1.77 at 27° C. This latter value differs rather much from that which holds for the saponification of esters by means of acids. The temperature coefficient of these reactions was determined by Price. The proportion reduced to 300° absolute and a 10° interval is about 1 to 2.35 for ethyl acetate and does not differ much for the other esters.

The experiments of Kremann give about as high values of the said proportion as that found for cane sugar, namely 1 to 4.1 for the formation of $C_2H_5HSO_4$

in the absence of water and 1 to 4 for the formation of ethyl ether from C_2H_5OH and $C_2H_5HSO_4$. In aqueous solution the first proportion sinks to 1 to 2.5—all figures reduced to 300° absolute. (The experimental error is in these cases rather great.)

At low temperatures the increase goes on very rapidly with temperature. Thus Plotnikow found for the said proportion at − 90° 1 to 6.2 for the reaction

$$C_2H_4 + Br_2 = C_2H_4Br_2.$$

If the said figure is reduced to 300° absolute it gives the proportion 1 to 1.97.

Therefore van't Hoff's rule, stating that the order of magnitude of the increase of velocities of reaction in an interval of 10° is always the same for ordinary reactions, is much nearer to the truth if all values are reduced to the same temperature, *e. g.*, to 300° absolute.

We may express this rule more simply in other words by saying that the constant A of the formula above (p. 124) is of the same order of magnitude for different reactions. We find for cane sugar and ethyl acetate saponified by bases or by acids 12,820, 5,580 and 8,700 respectively.

There are some very remarkable exceptions to van't Hoff's rule. The first is the decay of radioactive substances, which is independent of the temperature so that $A = 0$. The second is the solution of metals in dilute acids. Ericson Aurén determined the velocity of reaction when zinc dissolves in 0.1 normal hydrochloric acid. He found that it increased only 3 per cent. when the temperature rose from 9° to 50° C. This increase falls absolutely within the experimental

errors. In more concentrated solutions of the acids a greater increase in the velocity of reaction with temperature is observed, according to the experiments of Guldberg and Waage. The velocity of reaction at 18° compared with that at 0° in hydrochloric acid was found by them to be

for 1.3*n*. HCl	1.58
2 *n*. HCl	1.68
2.6*n*. HCl	1.70
4 *n*. HCl	2.44
8 *n*. HCl	3.25

Spring dissolved iceland spar with natural surfaces of cleavage in 10 per cent. HCl (about 3-normal) and found that the velocity of reaction increases to about double its value in 20 degrees (at 25° C.). This figure agrees very closely with that found for the solution of zinc in hydrochloric acid of the same strength. If the crystals were cut with surfaces parallel with or perpendicular to the chief axis the rate of increase with temperature was higher (about as 1 to 3 between 15 and 35) but rather irregular.

Recently I investigated the velocity of the solution of the active deposit from actinium emanation in water and 0.001 normal acetic acid at 15° and at 62° and found no appreciable difference at the two temperatures.

The photochemical reactions are only to a very insignificant degree dependent on the temperature in regard to their velocities. Thus for instance the ratio of increase in an interval of 10° was found to be for the following reactions (the table is taken from Plotnikow's Photochemistry).

Polymerization of anthracene.....1 to 1.21
Oxidation of quinine by means of chromic acid...1 to 1.06

Reaction of chlorine on hydrogen.....1 to 1.21
Reaction of oxalic acid with ferric chloride.....1 to 1.01
Reaction of oxygen on hydriodic acid.....1 to 1.39
Transformation of styrol to metastyrol.....1 to 1.36
Oxidation of dioxide of sulphur with oxygen.....1 to 1.20
Reaction of oxalic acid and mercuric chloride...1 to 1.12
The photographic process with silver bromide gelatine.....1 to 1.00, to 1 to 1.03

The reaction evidently depends upon the absorption of the active light rays, which alters very little with temperature. Another peculiarity which is without doubt connected with the low coefficient of temperature is that the photochemical processes behave as if they were monomolecular. Thus Bodenstein observed that hydriodic acid, which at high temperatures is decomposed according to the equation:

$$2HI = H_2 + I_2$$

which reaction is in fact found to follow the laws valid for bimolecular reactions, nevertheless on decomposition by means of light at low temperature obeys the equation:

$$HI = H + I,$$

i. e., behaves as a monomolecular reaction.

From this we conclude that each molecule of HI independently of other similar molecules is decomposed by the light waves. These tear asunder the molecules by the intensity of their vibrations, whereas at high temperature bonds connecting the atoms H and I in the molecule HI are weakened, so that a dissociation takes place at first after the impact of another molecule of HI, when there is an opportunity for the atoms H and I to combine with another atom of H or I respectively.

Another exception to the rule of van't Hoff is found in the spontaneous decomposition of certain enzymes or similar substances such as hæmolysins. These latter are subject to an exceedingly high influence of temperature. Thus for instance Madsen and Famulener found for a hæmolysin contained in blood serum from a goat a value of $A = 99{,}200$, corresponding to an increase in the velocity of reaction in the proportion 1 to 2.6 per degree at 50°.* A little less was the influence of temperature on the destruction of tetanolysin and vibriolysin, A being 81,000 and 64,000 respectively. The destruction of 2 per cent. solutions of rennet, pepsin, invertase and trypsin also possess very high values of A, namely 45,000, 38,000, 36,000 and 31,000 respectively, corresponding to a doubling of the effect in a rise of the temperature of 1.5, 2, 2.1 and 2.4 degrees at about 60°.

On the other hand the reactions of these substances with other substances usually agree approximately with the saponification of ethyl acetate by means of bases in regard to their hastening by temperature. Sometimes they give rather low values of A, for instance the inversion of cane sugar by means of invertase has a value of $A = 4{,}500$ between 20° and 30°, 5,500 between 0° and 20° (Euler and Beth af Ugglas) and the precipitation of egg-white by means of precipitin only 3,150.

It is well worth noting that different vital processes such as the assimilation in plants, the respiration of plants, the cell division in eggs possess nearly the same

* This circumstance may, as Madsen remarks, be of use for the human body. After the toxin has entered the blood, the temperature rises sometimes 2–3 degrees—fever temperature—and the poison is destroyed about 10 times more rapidly than without the fever-heat.

value of A (between 6,000 and 8,000) corresponding to an increase in the proportion of about 1 to 2 for a rise of temperature of 10° C.

Regarding these enzymatic and life-processes the literature is collected in Immunochemistry by S. Arrhenius.

LECTURE VIII.

CONDUCTIVITY OF SOLUTIONS OF STRONG ELECTROLYTES.

As we have seen above, Kirchhoff as early as 1858 applied thermodynamics to equilibria in solutions. From the change of solubility with temperature he calculated the heat evolved at solution according to the equation of Clapeyron. Thus he found for one gram of ammonia gas at 20° 214 cal. and for one gram of sulphur dioxide at 20° 97.7 cal., using Bunsen's figures for the solubility of these gases. These calculated heats do not agree very well with those determined calorimetrically by Julius Thomsen, namely 494 cal. for 1 g. NH_3 and 120 cal. for 1 g. SO_2. Kirchhoff demonstrated that analogous considerations of the vapor tension of salt solutions lead to determination of the heat of solution of the salt and the heat of dilution of its solutions. Regarding this latter point he showed that the experimental evidence, that at high dilutions of salts a further addition of water has no thermal effect, leads to the conclusion that the relative lowering of the vapor tension of salt solutions does not change with temperature, which rule had been demonstrated experimentally by von Babo.

This work was continued by Guldberg in 1870 and by van't Hoff (1885) who introduced his law on the analogy of solution and evaporation.

These deductions concern the heterogeneous equilib-

rium between a gas or a solid substance in equilibrium with its solution. Much more important are the homogeneous equilibria. Horstmann had deduced the laws of these for the gaseous state and these are of course according to van't Hoff's law applicable also to dilute solutions.

Berthelot and Pean de S. Gilles had in 1862–1863 investigated the equilibrium between an alcohol, an organic acid and their products of reaction, water and ether. The reaction was allowed to take place either in a gaseous mixture or in a liquid, to which was in some cases added benzene or acetone. The results of this classical investigation regarding a homogeneous equilibrium were calculated in 1877 by van't Hoff and in 1879 independently by Guldberg and Waage. They found that for the combination of 1 molecule of ethyl alcohol with n molecules of acetic acid and m molecules of water, the following equation holds good:

$$(m + x)x = 4(1 - x)(n - x),$$

where x is the number of alcohol and acid molecules transformed into x molecules of ethyl acetate. This is exactly the form of equation which holds for the gaseous state and according to van't Hoff's law also for the dissolved state. Another example was the determination of the dissociation of nitrogen peroxide N_2O_4 into $2NO_2$. This equilibrium takes place as well in the gaseous as in the liquid state, in the latter case diluted with some organic solvent, such as chloroform. In such experiments of Cundall (1891) the rate of dissociation was determined colorimetrically. The experiments agree very well with the gas laws, as Ostwald proved a little later.

These applications of the theoretical laws were rather few, until Ostwald in 1888 demonstrated the applicability of Guldberg and Waage's law of equilibrium in the electrolytic dissociation of weak acids, which work was completed some years later by Bredig's work on the weak bases. The experimental material regarding more than 200 weak acids and more than 40 bases was absolutely unrivalled and the evidence of the dissociation theory was generally regarded as indubitable. But on the other hand we remember that Planck had at the same time as Ostwald tried to apply the gas laws to the electrolytic dissociation of salts without success. The same may be said regarding the strong acids and bases. For all these so-called strong electrolytes van't Hoff gave an empirical formula, namely:

$$\frac{1-\alpha}{v}K=\left(\frac{\alpha}{v}\right)^{1.5}.$$

α is the degree of dissociation and v is the volume in which one gram-molecule of the strong electrolyte is dissolved, K is a constant. Instead of the exponent 2, which is demanded by theory, van't Hoff introduced the exponent 1.5 which accords much better with the experiments in these cases. As there now exists a much greater number of electrolytes belonging to this class, than to that which obeys the gas laws, it has been rightly said that this deviation from the gas laws is really the weak point in the electrolytic dissociation theory. But for just this case by the help of a great number of rather simple empirical rules we are able to calculate the equilibria for these substances with a great degree of accuracy. As these play a very important role in nature, as well in the waters of the

sources, rivers, seas and oceans, as in the humors of the animal bodies or of the plants, I will enter a little closer upon this chapter.

The calculation of the dissociated part is performed very simply by taking the quotient of the molecular conductivity of the solution in question and that of the same electrolyte in infinite dilution, *i. e.*, the limit value to which the molecular conductivity tends with increasing dilution. This limit value may be written as the sum of two components, the one valid for the anion and the other for the cation. These values are determined by means of the migration numbers first determined by Hittorf and later improved by different investigators. They have at 18° the following values (according to Kohlrausch). K 64.6, NH_4 64.2, Na 43.5, Li 33.4, Ag 54.3, Rb 67.5, Cs 68, Tl 66.0, H 315, $\frac{1}{2}$Ba 55.5, $\frac{1}{2}$Mg 46.0, $\frac{1}{2}$Zn 46.7, $\frac{1}{2}$Pb 61.3, F 46.6, Cl 65.5, Br 67.0, I 66.5, NO_3 61.7, ClO_3 55.0, COOH 45, CH_3CO_2 33.7, OH 174, $\frac{1}{2}SO_4$ 68.4, SCN 56.6.

For organic ions Ostwald and Bredig have given a great number of measurements, which indicate that the conductivity generally decreases with the increasing number of atoms contained in the ion.

The conductivity of the different ions depends on the solvent and its temperature. An increase of the temperature augments the conductivity, so that that of the less conducting ion increases in a higher proportion than that of the better conducting one, *i. e.*, the different conductivities approach each other with increasing temperature as is seen from the following figures calculated from the experiments of Noyes and his pupils:

Ion Temp.	18	100	156	218	281	306° C.
K	64.6	206.5	312	412	502	560
Na	43.5	154.5	242	347	467	520
NH_4	65.2	207.5	315	428	—	—
Ag	52.3	183.5	295	402	501	549
½Ba	53.4	201.5	325	462	656	784
½Mg	55.9	177.5	287	427	—	—
H	313.5	642.5	772	852	877	864
Cl	65.5	207.5	313	413	503	560
H_2PO_4	24.5	87.5	158	—	—	—
NO_3	63.5	183.5	275	378	464	516
½SO_4	58.2	248.5	403	653	958	1165
CH_3CO_2	34.6	130.5	208	313	413	474
OH	173	339.5	593	713	—	—

These figures are very instructive. The ion Ag which at 18° C. has six times less conductivity than the H-ion reaches nearly 64 per cent. of the conductivity of H at 306°. The acetate ion CH_3CO_2 has five times smaller conductivity than the ion OH at 18° but reaches about 44 per cent. of it at 218°. Also minor differences as between K and Na diminish at higher temperatures as well as the proportion between the conductivities of chlorine or NO_3 and CH_3CO_2. An exception to this rule is found for the bivalent ions, which probably tend to reach double the value of that for monovalent ions, with increasing temperature. ½SO_4 has already reached this value at 306°, but the barium ion has at 306° only attained a value about 50 per cent. higher than that of the monovalent ions.

A peculiar property is that the dissociation diminishes with increased temperature, which is also true for most weak acids. The non-dissociated part $(1 - \alpha)$ follows a rule enunciated by Ostwald, namely that in not too concentrated solutions of equivalent strength it is proportional to the product $v_1 v_2$ of the valencies v_1 and

v_2 of the two ions. Noyes gives the following instructive table of $(1-\alpha)$ expressed in per cent.:

Type	Eq. per Lit.	18°		100°		156°	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
KCl*	0.04	12	12	15	15	17	17
KCl	0.08	15	14	18	17	21	20
$BaCl_2$, K_2SO_4	0.08	28	28	34	34	40	40
$MgSO_4$	0.08	55	56	68	68	81	80

Type	Eq. per Lit.	218°		281°		306°	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
KCl*	0.04	20	20	25	25	31	31
KCl	0.08	25	24	31	32	39	38
$BaCl_2$, K_2SO_4	0.08	51	48	65	64	74	76
$MgSO_4$	0.08	93	96	—	—	—	—

The exponent in the equilibrium formula, which by van't Hoff has been calculated to 1.5 was according to Noyes' experiments variable between 1.4 and 1.5 with an average value of 1.46. With the aid of this formula of the equilibrium it is possible to calculate the degree of dissociation at any concentration.

Noyes also stated a rule found by myself, namely, that the dissociation of each of two salts with a common ion in a mixture is just as great as the dissociation of each salt itself would be, if the concentration of the common ion were the same as in the mixture (the rule of isohydric solutions). An analogous rule may be used for a mixture of any number of salts. This rule has a higher degree of exactness than those given above.

With the aid of these simple rules it is possible to calculate the degree of dissociation for salts in general. Very significant is the rule that the exponent in the equilibrium formula is the same for all salts, independently of the number of ions into which they decompose.

* For the strong monovalent acids, HCl and HNO_3, and for the bases, NaOH and $Ba(OH)_2$, the quantity $(1-\alpha)$ is only about half as great as for the salts of the same type.

The conductivity of the ions depends also in a high degree on the solvent medium. Thus for instance the conductivities at 18° in 0, 50, 80 and 100 p. c. solutions of alcohol are the following:

Per Cent. Alcohol.	K	Na	NH_4	H	OH
0	65.3	44.4	64.2	318	174.9
50	21.8	17.0	—	95.8	—
80	18.4	14.0	17.9	50.2	26.1
100	21.5	14.5	20	32.1	16.5

Cl	$(C_2H_5)_2NH_2$	Salicylat.	Acetate.	CH_3CNCOO	I
65.9	36.1	32	38.3	36.5	66.7
23.2	—	12.0	—	14.0	22.6
17.1	12.2	11.3	12.2	14.0	19.1
23.8	12.6	12.6	12.4	15.0	27.5

Most of these determinations were made by Godlewski, that regarding OH by Hägglund.

All the ions, except H and OH, possess a minimum of conductivity at a certain concentration of the alcohol. This minimum is found at different percentages of alcohol; for Cl, I, K and Na at about 85 per cent., for the salicylate ion at about 75 per cent. and for the cyanacetate ion at about 70 per cent. Probably this minimum depends upon the decrease of the fluidity with decreasing strength of the alcohol until it reaches 40 per cent., where the fluidity has its minimum at 18°. Evidently the minimum of conductivity does not coincide with that of the fluidity, but there is another factor which has a still greater influence.

The figures for H and OH in pure alcohol are very interesting, their conductivities being of the same order of magnitude as that of other ions. The hydrogen ion has also in alcohol the greatest conductivity, but is not very much superior to iodine and chlorine; one might expect this position of the hydrogen according to

its low atomic weight. The hydroxyl-ion falls far below all the ions consisting of simple atoms and also, curiously enough, below NH_4. This circumstance, as well as the strong increase in the conductivity of the H- and OH-ion with the addition of small quantities of water, in spite of the increased viscosity, indicates that the exceptionally great conductivity of these two ions in water is probably due only to the fact that they are the two ions into which water is electrolytically decomposed.

According to Godlewski's figures the conductivities of Na, K and Cl in alcoholic solutions containing from 0 to 100 per cent. alcohol are the following at 18° C.:

Per Cent. Alcohol.	Cl	Na	K	Mean.	H Obs.	H Red.	OH Red.	Fluidity.
0	1	1	1	1	318	318	174.9	1
10	0.766	0.781	0.766	0.771	234.6	307	—	0.689
20	0.583	0.605	0.559	0.582	188.7	324	—	0.476
30	0.473	0.516	0.449	0.479	147.7	308	—	0.381
40	0.401	0.427	0.361	0.396	120.1	303	—	0.348
50	0.354	0.379	0.334	0.356	95.8	269	—	0.354
60	0.307	0.339	0.303	0.316	75.9	240	—	0.375
70	0.275	0.317	0.299	0.297	62.2	209	—	0.431
80	0.261	0.312	0.282	0.285	50.2	176	91.6	0.510
90	0.261	0.307	0.288	0.285	40.6	143	—	0.625
100	0.363	0.324	0.329	0.339	32.1	95	48.7	0.831

The conductivity of the three monovalent salt ions sinks at first rapidly, reaches 50 per cent. at about 28 per cent. alcohol, 33.3 at about 56 per cent., then sinks slowly to a minimum of about 28 per cent. at 85 per cent. alcohol and then rises again to about 34 per cent. at 100 per cent. alcohol. If we correct the values of Godlewski for H tabulated under H obs. by dividing them by the mean values giving the conductivity of monovalent monoatomic salt ions, we might expect to find a constant value

if the influence of alcohol were the same on the H-ion as on K, Na and Cl, but, instead of that we get the figures under H red. These last figures remain nearly constant until 40 per cent. of alcohol are added—they decrease slowly, but only to the extent of 5 per cent. and thereafter they sink with a mean value of 32 units (10 per cent.) for each step of 10 per cent. of alcohol added until 90 per cent. of alcohol is reached. Thereafter for the last 10 per cent. of alcohol the decrease is not less than 48 units (15 per cent.). The few figures for OH, treated in the same manner, give a decrease between 80 and 100 per cent. of alcohol, which is nearly in the same proportions as the corresponding decrease for the figures under H red.

This observation may be explained in the following manner. The wandering of the ions is hampered by their collision with molecules (of water or alcohol). The ions H and OH behave exceptionally in water because when, for instance, an H-ion hits a water molecule HOH on its OH-side it may unite with the OH and set the H-ion of the water molecule free so that it may continue to carry away positive electricity. It is just as in the Grotthuss' chain, except that it is not necessary that the molecules turn around. If another ion than H or OH hits the water molecule, the effect of an exchange with the H or OH in a water molecule would be the same as a decomposition of the water into H- and OH-ions, which would be accompanied by a rise of the free energy, which is impossible. As the alcohol acts as an entremely weak acid, *i. e.*, may give the ions H and C_2H_5O, perhaps the high conductivity of H in alcohol may be partly explained by this circumstance,

but in all cases its superiority over other ions is so small that the ability of the alcohol-molecules to separate into their ions must be regarded as rather insignificant compared with that of the water molecules.

For the sake of comparison I have added to the above table the figures of the relative fluidity of alcoholic solutions. It has long been maintained that the conductivity is proportional to the fluidity. The change of both with temperature for weak salt solutions is very nearly the same, the fluidity increasing by about 2.4 per cent. per ° C. at 20°, which is very nearly the average temperature coefficient of the conductivity of dilute salt-solutions. Therefore G. Wiedemann, Bouty and F. Kohlrausch were inclined to regard these two temperature coefficients as identical and to maintain that the increase of the conductivity is due to the increase of the fluidity, which was further explained by the supposition that the ions were covered with a layer of water molecules and that this complex moved in the water. The main difficulty with this hypothesis was that the conductivity of acids and of bases increases much less, about 1.6 and 2.0 per cent. per ° C. from 18 ° C. on, respectively. The increase in the conductivity is here less than that of the fluidity. The same is valid for the salts. According to Noyes the values of the conductivity and that of the fluidity are at the temperatures 18°, 100° and 156° the following, if that at 18° is taken as unity.

	Λ at 18°	18°	100°	156°
Fluidity (f)		1.000	3.717	5.894
HCl	379	1.000	2.243	2.863
NaOH	216.5	1.000	2.743	3.856
$Ba(OH)_2$	222	1.000	2.905	3 815

	Λ at 18°	18°	100°	156°
KCl	130.1	1.000	3.183	4.805
NaCl	109.0	1.000	3.322	5.092
$AgNO_3$	115.8	1.000	3.168	4.921
$NaCH_3CO_2$	78.1	1.000	3.648	5.761
BaN_2O_6	116.9	1.000	3.294	5.133
K_2SO_4	132.8	1.000	3.426	5.388

As is seen from these figures the fluidity increases more rapidly than the molecular conductivity Λ of extremely attenuated solutions, which are considered here.

This behavior seems to be general, as soon as the solvent is not too much changed. The trivalent La-ion forms an exception according to Johnston, the quotient Λ/f increasing from 640 to 675 in the interval, 18° to 156°. The same is the case for bivalent ions as $\frac{1}{2}Ba$ and $\frac{1}{2}SO_4$ as is seen from the figures by Noyes given above. Also in the table above for small additions of alcohol (not exceeding 40 per cent.), the fluidity decreases much more than the conductivity of the ions Cl, Na and K. I have proved the same to be valid for small additions of different organic substances to water. The different electrolytes are not influenced in the same degree and therefore I have divided them in four groups: (1) strong acids and bases, (2) salts of two monovalent ions, type KCl, (3) salts of monovalent cations with divalent anions, type K_2SO_4, (4) salts of divalent cations with monovalent anions, type $BaCl_2$. The experimental results are given in the following table in which $(A - 1)$ gives the increase of the viscosity and α the increase of resistance in per mille at 25° on exchange of water to the quantity of 1 volume per cent. of the solution for the following substances, so that the volume remains the same.

	Fluidity.	1st Group.	2nd Group.	3rd Group.	4th Group
Acetone	19	15.6	16.2	19.0	16.7
Methyl alcohol	21	16.2	17.5	19.2	18.0
Ethyl ether	26	16.3	19.9	21.4	20.9
Allyl alcohol	26	18.8	—	21.2	21.1
Ethyl alcohol	30	18.8	23.4	25.1	23.9
n-Butyl alcohol	30	18.4	22.6	27.9	24.1
Isoamyl alcohol	31	17.2	21.6	27.3	26.7
n-Propyl alcohol	32	19.5	—	27.8	27.0
Isobutyl alcohol	33	19.5	24.4	28.0	26.5
Glycerol	33	20.5	22.7	26.0	25.0
Isopropyl alcohol	36	20.3	25.6	27.7	26.9
Dextrose	40	22.9	—	—	—
Galactose	40	23.2	—	—	—
Mannite	43	25.0	—	—	—
Cane sugar	46	24.4	29.9	33.4	30.9

With weak acids or bases and slightly dissociated salts, such as sulphates of divalent metals, etc., the dissociation is perceptibly diminished by even very small additions of organic substances. Then it happens that the conductivity changes in a higher degree than the fluidity.

Walden, on the other hand, investigated the molecular conductivity of extremely dilute solutions of tetraethylammonium iodide for 26 different solvents and found that it was proportional within 5 per cent. to the fluidity, as is indicated by the following table (valid for 25° C.).

	η	λ	$\lambda\eta$
Acetone	0.00316	225	0.711
Acetonitrile	0.00346	200	0.692
Acetylchloride	0.00387	172	0.666
Propionitrile	0.00413	165	0.682
Ethyl nitrate	0.00497	138	0.686
Methyl alcohol	0.00580	124	0.719
Nitromethane	0.00619	120	0.743
Methyl rhodanide	0.00719	96	0.690
Ethyl rhodanide	0.00775	84.5	0.655
Acetyl acetone	0.00780	82	0.640

	η	λ	$\lambda\eta$
Acetic acid anhydride	0.00860	76	0.654
Epichlorhydrine	0.0103	66.8	0.688
Ethyl alcohol	0.0108	60	0.648
Benzonitrile	0.0125	56.5	0.706
Furfurol	0.0149	50	0.745
Diethyl sulphate	0.0160	43	0.688
Dimethyl sulphate	0.0176	43	0.757
Nitrobenzol	0.0182	40	0.728
Benzyl cyanide	0.0193	36	0.695
Asymmetric ethyl sulphite	0.0238	26.4	0.628
Ethylcyanacetate	0.0250	28.2	0.705
Salicylaldehyde	0.0281	25	0.703
Formamide	0.0321	ca. 25	0.802
Anhydride of citraconic acid	0.0338	22.5	0.760
Anisaldehyde	0.0422	16.5	0.696
(Glycol	0.1679	ca. 8	1.32)
(Water	0.00891	112.5	1.00)

This value is not valid for the monovalent ions Cl, Na and K in ethyl alcohol at 18°; the product $\lambda\eta$ in this case is only 0.407 instead of 0.648. η is the viscosity, *i. e.*, the inverse value of the fluidity. Hence the limit values of the conductivities of extremely diluted solutions are not in a constant proportion, as has also been stated by Dutoit and Rappeport. In the table regarding the conductivities of ions the proportion between this magnitude in alcoholic and in aqueous solution is: for OH 0.094, H 0.101, NH_4 0.312, Acetation 0.324, Na 0.324, K 0.329, $(C_2H_5)_2NH$ 0.352, Cl 0.363, Salicylation 0.394, Cyanacetation 0.411, I 0.412 (Cf. p. 137).

It must be remarked that these figures are not in good agreement with those given by Dutoit and Rappeport. The discrepancies may serve as a proof of the difficulty of the measurements in non-aqueous solutions. The ions OH and H behave quite exceptionally, and OH in a higher degree than H which

may perhaps, as stated, be explained as due to a weak electrolytic dissociation of the alcohol molecules into H and C_2H_5O.

Dutoit and Duperthuis investigated the relation between fluidity and conductivity of NaI in different solvents at different temperatures. They found the following values of the limit value μ_∞ at 0° and the values of $\eta\mu_\infty$ at 0° and at 60°, where η is the viscosity:

	Ethyl Alcohol.	Propyl Alcohol.	Isobutyl Alcohol.	Isoamyl Alcohol.	Pyridine.	Acetone.
μ_∞ at 0°	27.95	11.85	5.48	4.49	42.10	12.75
$\eta\mu_\infty$ at 0°	0.495	0.453	0.441	0.374	0.573	0.502
$\eta\mu_\infty$ at 60°	0.457	0.443	0.397	0.269	0.562	0.517 (at 40°)

In all cases observed, except for acetone, $\eta\mu_\infty$ sinks with increasing temperature, which indicates that the conductivity changes less with temperature than the fluidity, just as for water, according to Noyes, and as for small additions of organic substances to water.

Schmidt and Jones found $\eta\mu_\infty$ for KI to be (at 18°) 0.72 in methyl alcohol, 1.32 in glycol and 2.10 in glycerol, which is the order of η in the three cases. Consequently the viscosity or the fluidity changes in a higher proportion than the conductivity.

Quite recently Walden has investigated the conductivity of salt solutions in different organic solvents at rather great intervals of temperature. He found that the conductivity can not be expressed as a linear function of temperature, as is done in most cases. The curve, which gives the conductivity as a function of the temperature as abscissa approaches the abscissa axis asymptotically, when the temperature sinks down towards the absolute zero. The same is true

also for the fluidity. The extrapolation formula which leads to a value zero as well for the conductivity as for the fluidity at a temperature above absolute zero, and which has for instance been used by Kohlrausch for determining this temperature for aqueous solutions to about $-30°$, fails absolutely at low temperatures. This had also been found for aqueous solutions of H_2SO_4, $CaCl_2$ and NaOH by T. Kunz in 1902.

Green and Martin and Masson investigated the conductivity μ_∞ of HCl, KCl or LiCl in water with the addition of cane sugar, so that the fluidity (f) changed in about the proportion 1 to 23. They found that a formula $\mu_\infty = kf^n$, where k is a constant, gives good results, n is found to be 0.5 for HCl and 0.7 for KCl or for LiCl. In other words the conductivity changes much more slowly than the fluidity, especially for the acid, which agrees wholly with the behavior of aqueous solutions, when the fluidity changes with temperature.

Similar experiments have been made by Pissarshewski and Schapowalenko on solutions of $KAgC_2N_2$ and KBr in methyl or ethyl alcohol, mixed with different quantities of glycerol. The μ_∞ increases at 25° about in the proportion of 1:400 and 1:200 respectively if the solvent changes from pure glycerol to pure methyl and ethyl alcohol respectively, whereas $\eta\mu_\infty$ instead of being constant simultaneously decreases in the proportion 3.5:1 and 3.7:1 respectively. This corresponds to a value of n = about 0.8 and 0.75. At 45° the value of n increases by about 0.05.

A similar rule seems to hold also for fused electrolytes according to Goodwin and Mailey. They examined nitrates of lithium, sodium, potassium, and silver

at temperatures up to 500°. The conductivity is not strictly proportional to the temperature, but increases less and less rapidly as the temperature rises. The product $\eta\lambda$ at different temperatures is nearly constant for KNO_3, $K_2Cr_2O_7$ and mixtures of KCl and NaCl, but decreases (just as for aqueous solutions) with rising temperature by 10 per cent. for $LiNO_3$ between 250 and 300°, by 4.2 per cent. for $AgNO_3$ between 250 and 350° and by 6.4 per cent. for $NaNO_3$ between 350 and 450°.

The conductivities of fused salts have also been measured by Arndt and Gessler, from whom the following table with some slight extrapolations indicated by brackets is reproduced. The conductivity is given in reciprocal ohms per cm. length and cm.^{2} cross-section.

Temp ° C.....	500	600	700	800	900	1000	1100
$CaCl_2$.....	—	—	—	1.90	2.32	2.66	(2.86)
KCl.....	—	—	—	2.19	2.40	2.61	—
KBr.....	—	—	(1.55)	1.75	1.95	(2.15)	—
KI.....	—	—	1.39	1.64	—	—	—
NaI.....	—	—	2.56	2.70	2.83	(2.97)	—
AgCl.....	4.20	4.48	4.76	4.98	5.14	—	—
AgBr.....	3.02	3.18	3.34	3.50	3.68	—	—
AgI.....(2.40)		2.52	2.64	2.72	—	—	—
$NaPO_3$	—	0.30	0.55	0.80	1.05	1.30	1.54
B_2O_3.....	—	—	—	7.10^{-6}	21.10^{-6}	46.10^{-6}	—
NaCl.....	—	—	—	3.34	3.66	(3.98)	
$SrCl_2$.....	—	—	—	—	1.98	2.29	2.57

The conductivity increases very regularly and rather slowly with temperature except for B_2O_3, the dissociation of which evidently increases very rapidly with temperature. The conductivity of KCl or NaCl is very nearly proportional to the absolute temperature, that of KI and KBr increases a little more rapidly, still more that of $NaPO_3$, $CaCl_2$ and $SrCl_2$, that of NaI

and the silver salts more slowly. The conductivity of mixtures of equal quantities of $CaCl_2$ and $SrCl_2$ is very nearly equal to the mean value of the conductivities of the two components. For mixtures of KCl and NaCl the conductivity was a little less (1.5 to 3 per cent.) than calculated according to the said rule. For mixtures of $NaPO_3$ (x per cent.) and B_2O_3 the following values were observed at 900° (d is density, c concentration in gram equivalents per liter, Λ equivalent conductivity, η viscosity):

x	0	0.5	1	5	10	25	50	100
d	1.520	1.522	1.552	1.585	1.655	1.820	2.115	2.144
c	——	0.075	0.15	0.78	1.62	4.46	10.35	21.0
Λ	——	0.67	——	1.55	——	——	16.4	49.5
$\eta\Lambda$	——	74.3	——	73.3	——	——	73.8	74.3

The product $\eta\Lambda$ is very nearly constant. From this result the authors conclude that probably the $NaPO_3$ is nearly totally dissociated into its ions. Goodwin and Kalmus also found $\eta\Lambda$ for fused $PbCl_2$, $PbBr_2$ and $K_2Cr_2O_7$, nearly independent of temperature and thence concluded that fused salts are subject to a high degree of electrolytic dissociation.

The concentration and equivalent conductivity at 900° of some salts is given below:

Salt	KCl	NaCl	$CaCl_2$	$SrCl_2$	$BaCl_2$
c	19.7	25.3	36.2	34.0	30.5
Λ	123.5	144.5	64.1	58.2	56.1

The molecular conductivity, which for $CaCl_2$, $SrCl_2$ and $BaCl_2$ is 2Λ, is of the same order of magnitude for the five fused salts.

A great number of investigators have found that in some cases solutions behave so "abnormally" that the molecular conductivity instead of increasing de-

creases with dilution. For aqueous solutions this irregularity has been observed with highly diluted solutions of strong acids and bases and is explained as due to the presence of traces of impurities, especially carbonic acid, in the distilled water, used for the dilution. A similar explanation seems impossible in most of the other cases observed with solvents other than water and they were therefore sometimes considered as a proof of the insufficiency of the theory of electrolytic dissociation. A clew to the understanding of these "abnormities" was found by Steele, McIntosh and Archibald, who investigated the conductivities of solutions of organic substances such as ethyl ether and acetone, in HCl, HBr and HI. They made it probable, that some molecules, two or three, of the dissolved substance combine with one molecule of the solvent to form a salt-like conducting compound. According to the law of chemical equilibria the number of conducting molecules d minishes with increasing dilution. Hence the increased dissociation of the conducting molecules with increasing dilution may be more than compensated by their increasing decomposition. The said authors also applied this idea to similar cases observed before by other investigators.

Similar observations were made by I. Wallace Walker and F. Godschall Johnson on solutions of KCl, KI and KCN in acetamide. They also observed the migration of the ions in these cases and found that combinations of the salts and the solvent occurred.

Some very instructive similar observations have been made by Foote and Martin. They found the following values of the molecular conductivity μ at 282° C. for solutions of 1 gram-molecule in V liters of $HgCl_2$:

$V=$	2	5	15	20	30
μ for CsCl	—	70	51	48.5	44
μ for KCl	81	62	45.7	43.4	38.5
μ for NH_4Cl	—	64.5	46.5	—	—
μ for NaCl	61.5	43.8	31.3	28.0	—
μ for CuCl	70	42	26	24	—

$CuCl_2$ is soluble but does not increase the conductivity of the solvent.

Determinations of the freezing point of the solutions indicated that the depression was normal. It was therefore necessary to suppose that molecules of, *e. g.*, the composition $HgCl_2 . Na_2Cl_2$ were formed which dissociate into the ions Na and $NaHgCl_4$. The presence of similar double salts and complex ions in solutions have been ascertained in many different ways, as for instance the solubility of $HgCl_2$ or HgI_2 in solutions of KCl or KI, the freezing point of such complex solutions, the diminution of the catalytic influence of KI on H_2O_2 on addition of HgI_2, the distribution of HgI_2 between a solution of KI in water and benzene. They are very well known in crystalline form. This is a good example of the applicability of the hypothesis of Steele, McIntosh and Archibald.

Another series of interesting measurements of abnormal dissociation has been given by Walden and Centnerszwer for solutions of potassium iodide in sulphur diox de. They found:

$V=$ 0.5	1	2	4	8	16	32
$\mu=38.2$	42.9	44.9	42.0	35.6	37.0	41.3
$V=64$	128	256	512	1,024	2,048	
$\mu=48.3$	57.5	70.4	86.7	105.5	126.0	

At first μ increases in the normal manner, then decreases until a minimum 35.6 is reached at $V = 8$ and thereafter increases very rapidly again.

This field was in a high degree elucidated by Franklin and his pupils. They investigated solutions of a great number of salts in ammonia and organic amines. As an example I give the figures for the solution in NH_3 of ammoniacal zinc nitrate $ZnN_2O_6 + 4NH_3$ at $-33.5°$.

$V =$	0.999	1.539	1.961	2.520	3.051	3.891	7.717
$\mu =$	98.8	103.6	102.0	99.48	97.34	93.42	86.52
$V =$	15.25	30.10	59.46	117.6	182.2	358.0	707.2
$\mu =$	86.30	94.78	105.8	124.3	136.0	160.8	191.0

Similar cases, with first a maximum, thereafter a minimum and then a normal increase is found for solutions of copper nitrate, potassium mercuricyanide and potassium amide in ammonia and silver nitrate in methylamine. In other cases (*e. g.*, $AgNO_3$, $LiNO_3$, NH_4NO_3 or KI in NH_3) the first maximum disappears and is replaced by an inflexion point and thereafter an interval of nearly constant values of μ. In still other cases, *e. g.*, trimethylsulfonium iodide, metamethoxybenzenesulfonamide, orthonitrophenol, trinitraniline, the behavior was just the same as the normal one in aqueous solutions.

The first increase at low values is due to a rapid increase in the flu dity on addition of ammonia, the maximum with the following decrease is due to formation of molecular complexes. It is noteworthy that this maximum is most obvious just for solutions of salts of heavy metals, which as early as 1859 were found by Hittorf to contain complex ions, especially in organic solvents (ethyl and amyl alcohol). They are also known to give complex salts with ammonia. After the minimum, the quantity of ammonia is so great that its concentration may be regarded as nearly constant;

then the concentration of the conducting compound of ammonia and salt is nearly proportional to the quantity of salt and the conductivity increases in a regular manner. Two different compounds occur in these cases, one containing a less percentage of ammonia and a better conductor (in high concentrations of the salt), and one combined with a greater quantity of NH_3 and a poorer conductor (at greater dilutions). The abnormality with the minimum may then simply be due to the greater friction of the more voluminous ions rich in NH_3 as compared with that of the ions combined with smaller quantities of ammonia, just as the friction of organic ions increases with their complexity.

A Russian chemist A. Ssacharow investigated solutions of NH_4I, LiI, $AgNO_3$ and two bromides of amides in aniline, mono- and dimethylaniline and observed some cases in which μ decreased with increasing dilution. Evidently these solutions are very nearly related to those observed by Franklin.

After the interesting and wide-reaching investigations of Franklin similar older observations of Kahlenberg and Ruhoff regarding the abnormal conductivity of solutions of silver nitrate in amylamine are easily understood. The assertion made by these authors, that these abnormal conductivities are incompatible with the dissociation theory, is therefore eliminated.

Even in fused electrolytes complex salts are formed, which must be taken into account in calculations regarding their conductivities. Thus R. Lorenz in experiments regarding the migration of ions found that in molten mixtures of $PbCl_2$ and KCl there exist compounds $2PbCl_2 . KCl$, $PbCl_2 . 2KCl$ and $PbCl_2 . 4KCl$.

One of the most experienced investigators regarding non-aqueous solutions, the Italian chemist Carrara, comes to the final conclusion that the same laws are valid for these solutions as for the aqueous ones and that the conclusions of the dissociation theory are applicable and can explain all seeming discrepancies in the one case as well as in the other. Another of the most experienced men in this field, Walden, has expressed the same opinion in nearly identical words.

LECTURE IX.

EQUILIBRIA IN SOLUTIONS.

THE simplest chemical equilibrium is that between a gas and its solution in a fluid, which is expressed by Henry's law, discovered in 1803. This law states that at a given temperature the concentration of the absorbed gas in the fluid phase stands in a constant proportion to that of the gas in the gaseous phase. For highly soluble gases as NH_3 or CO_2 the law is not exact.

A similar law was enunciated by M. Berthelot and Jungfleisch for the partition of a dissolved substance between two liquid phases for instance iodine between bisulphide of carbon and water for which they found (at 18° C.)

Gram I in 100 c.c. water per cent.	0.041	0.032	0.016	0.010	0.009
Gram I in 100 c.c. CS_2 per cent.	17.4	12.9	6.6	4.1	0.76
Ratio	1:424	1:403	1:412	1:410	1:400

If the iodine is present in so great quantity that it is not wholly soluble in the two fluids, concentrated solutions are formed and the ratio is equal to the quotient between the solubility of iodine in water and that in bisulphide of carbon. This remark was made by Berthelot.

Through experiments regarding the freezing point of solutions it has been proved that a substance, dissolved in two different solvents, generally possesses different molecular weights in the two cases. In such circum-

stances the simple law of Berthelot and Jungfleisch does not hold. Nernst improved it by attaching the condition that the law is true for only the same kind of molecules. If for instance benzoic acid in water consists (chiefly) of simple molecules C_6H_5COOH and in benzene (chiefly) of double molecules $(C_6H_5COOH)_2$, then the chemical equilibrium prevails:

$2C_6H_5COOH$ (in water) $\leftrightarrows$ $(C_6H_5COOH)_2$ (in benzene)

and the law of Guldberg and Waage demands:

(concentration in water)^2 = constant (concentration in benzene).

This also agrees well with experience as indicated by the following figures (valid at 20°).

Conc. in water c_1	0.0976	0.1500	0.1952	0.289	(g. in 100 c.c.).
Conc. in benzene c_2 =	1.05	2.42	4.12	9.7	
Constant $= c_2 : c_1^2$	=110	108	108	116	

For more dilute solutions the number of electrolytically dissociated molecules in the aqueous solution and of simple molecules in the benzene solution increases, and the equilibrium cannot be calculated in the simple manner given above, but a closer analysis is necessary. The equilibrium is also disturbed by the circumstance that a small quantity of water is soluble in the benzene and vice versa, and this quantity depends on the concentration.

The said law has been of great use in determining the partial pressure of a dissolved substance in a solvent, which itself possesses a perceptible vapor pressure, for instance of water in ethyl ether, further for determining equilibria, for instance between NH_3 and NH_4OH in aqueous solution. If namely this is shaken with chloroform, the NH_3 molecules are divided

between the water and the chloroform, but the NH_4OH molecules occur only in the aqueous solution. Moore used some figures of Dawson and MacCrae in which the concentrations were the following, c concentration of ammonia in the aqueous phase, c_1 concentration in the chloroform phase, x concentration of NH_3 in the aqueous phase, y concentration of NH_4OH in the aqueous phase, the concentration of the ions is so small that it might be omitted. The temperature is written under t.

t	c	c_1	x	$x:c_1$	y	$y:x=k_2$
10°	0.3917	0.01352	0.213	15.8	0.178	0.836
20°	0.3917	0.01588	0.251	15.5	0.141	0.560
30°	0.3917	0.01846	0.285	15.4	0.106	0.372

The ratio $y : x$ is here constant at a given temperature and the determination of x is therefore not possible simply by changing c. Therefore experiments at different temperatures were necessary. According to the law of van't Hoff regarding the change of equilibrium with temperature it is possible to determine the change of the ratio of y/x with temperature, if we know the heat evolved on the addition of NH_3 to H_2O so that NH_4OH is formed. Moore made it probable that $x : c_1$ does not change with temperature which is found to be true in this and similar cases, *i. e.*, that no perceptible heat is evolved, when in the experiment NH_3 passes from an aqueous solution to a chloroform solution. This gives a means of determining the ratio $y : x$. (Moore started from a little different premises and therefore did not find $x : c_1$ absolutely constant.) As is seen from the table above the ratio $y : x$ decreases rapidly corresponding to a heat of hydration of ammonia equal to 7,190 calories. The dissociation con-

stant was found to be about $k = 5.10^{-5}$ at 20° in the equilibrium equation $ky = z^2$, where z is the concentration of the ions NH_4 and OH. This constant k is evidently $(1 + k_2) : k_2$ times greater than that found if instead of the concentration y of NH_4OH, as is generally done, is put the concentration $x + y$ of NH_3 and NH_4OH together.

The law of partition also enables us to determine the molecular weight of substances in solid solution. For instance thiophene is soluble in solid and in liquid benzene and the partition coefficient is independent of the concentration, from which we conclude that its molecular weight is the same in both cases. Other experiments have been carried out with partition of ethyl ether between water and solid naphthalene and it was found that the molecules of ether in naphthalene correspond to double the magnitude of that given by the chemical formula.

Another instance of the use of the partition law is found in studying the distribution of substances between cells, *e. g.*, bacteria or blood-corpuscles and the surrounding solutions. In this manner I have found that ammonia or acetic acid or saponine possess the same molecular weight in water and in red blood-corpuscles. We can not decide if the said reagents are united with some substance in the blood-corpuscles but we know that in every molecule of the compound just as much of the reagent is present as in one molecule of it in the surrounding solution. That they are bound to some substance in the blood corpuscle is to a certain degree probable because their concentration in it is between a hundred and a thousand times greater than in

the liquid in which it is suspended. The same is true for the absorption of so-called agglutinins in just those bacteria which are sensitive to them and of so-called immune-bodies in red blood-corpuscles. In these two cases a high degree of specificity prevails so that only a certain agglutinin is in a higher degree absorbed by a given bacterium, *e. g.*, coli-agglutinin by Bacterium coli, cholera-agglutinin by cholera-vibrions and a certain kind of red blood-corpuscles takes up a given immune-body, namely corpuscles from that species of animals, by the injection of whose corpuscles in the veins of another animal the immune-body in question has been produced. This specificity can scarcely be understood without supposing a chemical reaction of the cell-content with the reagent. In this case the compounds formed contain only two thirds as much of the reagent, as a molecule of it in the surrounding fluid. It was urged by the school of colloid chemists, that the equation of equilibrium in this case:

$$A = K \,.\, C^{0.67},$$

where A is the concentration of the absorbed substance, C its concentration in the surrounding fluid, indicates that an adsorption phenomenon prevails here. This might be true for a small variation of C, but in the present case the equation holds for so great variations of C as in the proportion 1 to 300 or more of which there is no example in the adsorption phenomena, except perhaps at very small concentrations, where proportionality rules between A and C.

The most important of all equilibria between dissolved substances is that proved for weak acids by

Ostwald. The law of mass action does not only hold for weak monobasic acids as acetic acid, but as well for weak di- or poly-basic acids, such as tartaric acid or citric acid. These acids are so weak that only one of the hydrogen ions is dissociated off from each molecule, or at least the molecules from which two hydrogen ions are dissociated away are so small in number that they may be wholly neglected.

But still there were some among the weak acids, such as the amidobenzoic acids, picolic acid, etc., for which the so-called dissociation constant in the equation of equilibrium is not constant but changes rather rapidly with dilution. Ostwald himself supposed that perhaps the explanation ought to be sought for in the circumstance that these acids may also act as weak bases, so that a salt-like compound might be formed from the two molecules of the acid.

Such substances which may act as acids towards bases or as bases towards acids, are called amphoteric electrolytes. The simplest of them is water, which dissociates into the hydrogen ion characteristic for acids and the hydroxyl ion characteristic for bases. Most of these substances are amido acids, in which one hydrogen atom of an acid is replaced by the group NH_2 or a pyridine residue or something similar. Also some hydrates of metals are amphoteric, *e. g.*, those of lead, aluminium, zinc, chromium, arsenic, beryllium, tin, tellurium, germanium. These last substances have the formula R . O . H, which gives H-ions as well as OH-ions. The amino acids possess the formula NH_2RCOOH of which a part is united with H_2O to $OH . NH_3$-$RCOO . H$ just as a part of NH_3 is bound to H_2O,

thereby giving NH_4OH. The molecule $OH . NH_3$-R . COO . H is the amphoteric electrolyte; it may dissociate off hydroxyl-ions from its NH_3 side and H-ions from its COO-side. It may even give off both and then be regarded as an "inner salt." Bredig was the first to study these interesting substances and he induced his pupil Winkelblech to continue this investigation. They used the conductivity and the hydrolysis of the salts of these electrolytes to determine the dissociation constants of the two sides of these molecules. These researches were carried much further by James Walker, who gave the method for rationally calculating the degrees of dissociation and conductivities of these substances. Finally Lundén has performed an elaborate experimental work and written a monograph regarding them. As an instance I reproduce the following table regarding meta- and ortho-aminobenzoic acid (at 25°).

META-AMINOBENZOIC ACID.

v.	$a.10^5$	$d.10^5$	$k.10^5$ calc.	$k.10^5$ obs.
64	11.8	159.0	1.12	1.12
128	11.4	77.0	0.87	0.88
256	10.7	36.2	0.81	0.84
512	9.6	16.2	0.88	0.91
1024	8.2	6.8	1.02	1.07

ORTHO-AMINOBENZOIC ACID.

v.	$a.10^5$	$d.10^5$	$k.10^5$ calc.	$k.10^5$ obs.
100	21.4	24.7	0.69	0.69
200	17.6	10.1	0.80	0.81
500	12.5	2.8	0.92	0.93
1000	9.2	1.0	0.98	1.02

In these tables a represents the concentration of the H-ions, d that of the molecule in question with the ion OH thrown off (the number of the OH-ions present is determined by the circumstance that the product of

the concentration of the H-ions with that of the OH-ions is constant = k_w, *e. g.*, $0.31.10^{-14}$ at 10°, 10^{-14} at 25°, $5.5.10^{-14}$ at 50°), v is the volume in which one gram-molecule is diluted, and k is the apparent dissociation constant calculated from the conductivity under the supposition that the two acids behave as other acids. The meta-acid was measured by Winkelblech and calculated by Walker, the ortho-acid was measured and calculated by Lundén.

It is obvious from the tables, that the "dissociation constant" k is not constant, but also that this agrees wholly with theory. The dissociation constant is really double, one for the hydrogen-ions, called k_a (the substance regarded as an acid) and one for the OH-ions, called k_b (the substance regarded as a base). These two constants were: for the meta-acid $k_a = 1.63.10^{-5}$ and k_b $1.23.10^{-11}$, for the ortho-acid $k_a = 1.06.10^{-5}$, $k_b = 1.37.10^{-12}$. They are therefore much stronger as acids than as bases. The observed k is rather smaller than the real k_a; the amphoteric character lowers the dissociation of H-ions from the molecule. The meta-acid is stronger than the ortho-acid both as an acid and as a base. Rather remarkable is the fact that the concentration of H-ions for the meta-acid is nearly constant between $v = 64$ and $v = 256$, this is characteristic especially when k_b exceeds very much the value of k_w, the ion-product of water at the same temperature. For a value $k_a = 10^{-5}$ and $k_b = 1{,}000k_w$ Walker has calculated that a does not sink more than from $9.99.10^{-5}$ to $9.44.10^{-5}$ between $v = 1$ and $v = 100$, whereas d simultaneously sinks from $8{,}330.10^{-5}$ to 79.10^{-5}. If $k_a = k_b$ the amphoteric electrolyte is neutral, *i. e.*,

there are just as many H- as OH-ions in the solution. In this case the degree of dissociation is independent of the concentration and may be rather high, *e. g.*, for $k_a = 10^{-7}$ the degree of dissociation is 0.667, for $k_a = 10^{-9}$ only 0.019 (no such substance is yet known).

Most amphoteric electrolytes measured are stronger as acids, exceptions are : acetoxim $k_a = 6.0.10^{-13}$ and $k_b = 6.5.10^{-13}$ at 25°, $k_a = 9.9.10^{-13}$ and $k_b = 19.0.10^{-13}$ at 40° and histidin $k_a = 2.2.10^{-9}$ and $k_b = 5.7.10^{-9}$ at 25°. The albuminous substances, such as albumine from eggs or blood-serum, globuline, etc., seem also to be more acid than basic substances, they give salts more easily with bases than with acids. The same is the case with their decomposition products leucin, glycin, and alanin, for which k_a is about 100 times greater than k_b, and still more for tyrosin, leucylglycin, alanylglycin and glycylglycin, which are about 1,000 times stronger as acids than as bases. The peptones and still more casein are very decided acids, on the other hand the protamins, investigated by Kossel, are of a basic nature.

Robertson has made some interesting applications of the theory of amphoteric electrolytes on albuminous substances.

The chief objection, which could be made to the electrolytic dissociation theory at first glance, was the following. If two substances are mixed with each other, they may generally be separated from each other by means of diffusion. In this manner it was for instance possible to prove experimentally that sal-ammonia, NH_4Cl, is in the gaseous state partially decomposed into ammonia NH_3 and hydrochloric acid, HCl (v. Pebal). But it had never been observed that the ions, into which a

salt is supposed to be decomposed, may be separated through diffusion. This behavior depends on the circumstance that the ions of a salt, *e. g.*, NaCl, are charged with enormous quantities of electricity of opposite sign, Na with positive, Cl with negative electricity to the extent of 96,550 coulombs per gram equivalent. If therefore Na and Cl separated from each other, powerful electrical attractions between the Na and the Cl atoms would carry them back to each other, as I remarked in my inaugural dissertation. The two ions therefore move together in equivalent quantities through the fluid, as if no dissociation took place.

The diffusion of salts shows a certain parallelism with their conductivity, *i. e.*, with the mobility of their ions as has been especially emphasized by Long and Lenz. This question could not be cleared up, before it was regarded from the point of view of the dissociation theory, which was done by Nernst in his well-known investigation on the mechanism of the diffusion phenomenon. There he proves that the rate of diffusion is equal to the driving osmotic pressure divided by the sum of the frictions of the ions determined by means of experiments on their conductivities. In this manner he calculated the coefficients of diffusion and found them in very good agreement with the values determined experimentally. Later on Öholm has worked out this chapter with the best of success.

It may be remarked here, when we deal with the physical applications of the dissociation theory, that Nernst, proceeding further along the same lines calculated the electromotive forces, which arise through the unequal diffusion of the ions in so-called concen-

tration cells, which had been before treated thermodynamically by Helmholtz. In this case the powerful charges of electricity, which in a free solution hinder the unequal diffusion of the two ions, are carried away by means of unpolarizable electrodes dipping into the unequally concentrated parts of the solution and connected metallically with each other. The results found by Nernst by means of his kinetic views agree wholly with those arrived at by Helmholtz. Nernst's theory has been improved by the work of Planck and still more by the recent work of Pleijel, who has solved the problem in its entirety and removed the mathematical difficulties which hindered its complete solution at an earlier stage.

The theoretical study of the phenomenon of diffusion has led to a conclusion which seems very paradoxical. If hydrochloric acid diffuses in water, its diffusion constant is found to be 2.09 at 12° C., which also agrees very well with the theory of Nernst. If instead of using pure water for the diffusion, I take a solution of sodium chloride, I might expect that the molecules HCl moved, *i. e.*, diffused more slowly in that medium than in water because of the increase of the viscosity on addition of NaCl. But instead of that an increase of the constant of diffusion is observed. For instance into a cylindrical vessel was poured a layer of 1 cm. height of 1.04 *n* HCl and over it was placed pure water to a height of 3 cm. The diffusion constant was found to be 2.09 at 12°. In another experiment 0.1 *n* NaCl was used instead of water, so that at the bottom of the cylindrical vessel was a 1 cm. high layer 1.04 *n* in regard to HCl and 0.1 *n* in regard to NaCl and over it were placed 3 cm. of 0.1 *n* NaCl.

The diffusionconstant was now 2.50. According to Nernst's theory I calculated 2.43. In 0.67 *n* NaCl the constant was still higher 3.51, calculated 3.47. Many analogous experiments with results agreeing with the dissociation theory were performed with nitric and hydrochloric acid, caustic potash and soda.

The explanation is that when the H-ions (*i. e.*, the acid) diffuses in pure water they must drag the (about 5 times) more immobile Cl-ions with them in equivalent number. If now Na-ions are distributed in the same fluid, these ions are carried back in the opposite direction of the diffusing H-ions because of the electric forces which hold back the H-ions and pull on the Cl-ions in the direction of diffusion (upwards in the experiments). The driving back of the Na-ions partly neutralizes these electric forces, so that therefore the H-ions are not so strongly held back nor the Cl-ions pushed up as in pure water. Therefore the H-ions diffuse more rapidly and that in a so much higher degree as the Na-ions are more numerous relatively to the H-ions. The maximal velocity which the H-ions may reach at 12° is that corresponding to no hindrance from electrical forces and gives a diffusion constant 6.17. With 0.52 *n* HCl and 3.43 *n* NH_4Cl I reached a value of 4.67 instead of theoretically calculated 5.72.—It must be borne in mind that at these high concentrations the degree of dissociation of the HCl is diminished, which is not taken into consideration, and therefore the observed dissociation constant is smaller than the calculated one determined with the supposition that the electrolytic dissociation is complete.

This phenomenon is a so-called salt action, which can

not be explained, if we suppose the molecules of the diffusing acids or bases and the added salts not to be dissociated into electrically charged ions. It is a real proof of the electrolytic dissociation hypothesis.

As we have seen above, Guldberg and Waage, in their theoretical investigation of 1867, supposed that foreign subtances, such as salts, alcohol, etc., exert a certain influence on reactions without actively taking part in them, and they introduced into their formulæ different terms to account for this action. It was especially the velocity of reaction which was found to depend on the foreign substances. They found experimentally that some of the substances accelerate the reaction (*e. g.*, NH_4Cl the solution of zinc in HCl); others retard it (*e. g.*, $ZnCl_2$ in the same reaction). Van Name and Edgar found that KI increases the rate of solution of metals by means of iodine.

Through this introduction of new terms the equations of Guldberg and Waage lost their simplicity and the many empirical constants in them allowed the arrangement of a good agreement between theory and experience but thereby the correctness of the theory was not subject to a convincing proof. Therefore at a later stage they threw away the many terms and coefficients having reference to the foreign substances and the simple law, which now carries their name, was the excellent result. It is, of course, not exact for higher concentrations or if great quantities of foreign substances are added.

But nevertheless it has been proved that the salts exert a certain influence which is sometimes very great especially on the velocity of reaction. This may as

we now know be of rather different kinds and it was therefore quite natural that Guldberg and Waage were not able to disentangle this complicated riddle. The simplest case is the action of a sulphate such as potassium sulphate on sulphuric acid. Then a part of the acid is bound and the acid sulphate is formed. Therefore the catalytic action of the sulphuric acid is diminished by the addition of neutral sulphates. Spohr found that 1 n H_2SO_4 at 25° has a reaction constant equal to 21.34 in inverting cane sugar. On adding 0.5 n K_2SO_4 the constant decreased to 16.07 (*i. e.*, by 24.7 per cent.), on adding 1 n K_2SO_4 the constant was only 11.56 (decrease 45.8 p. c.).

Quite different is the action on strong monobasic acids. The velocity of inversion by means of 0.25 n HBr was by Spohr found equal to 9.67; an addition of 0.5 n KBr or 1 n KBr increased the constant to 12.18 (26 p. c.) and 15.48 (60.1 p. c.) respectively. This peculiar action will be treated in the next lecture (p. 179).

The greatest action is exerted on weak acids (*e. g.*, acetic acid) by their salts (*e. g.*, sodium acetate). In this case, if we have 1 gram-molecule of acetic acid with the degree of dissociation α and n gram-molecules of $NaCH_3COO$ with the degree of dissociation β in V liter solution, the following equilibrium holds:

$$\alpha(\alpha + n\beta) = K(1 - \alpha)V$$

where K is the constant of dissociation ($1.8.10^{-5}$) for acetic acid at the temperature used (25°). α is very small (less than 1 p. c.), β rather near unity. $1 - \alpha$ is very nearly constant (as 1). The greater n is, the less is α and the velocity of reaction, which is nearly pro-

portional to α. I found the following values of the velocity of reaction, ρ, when $V = 4$:

$n =$	0	0.05	0.1	0.2	0.5	1
$10^3\rho$ observed	= 0.75	0.122	0.070	0.040	0.019	0.0105
$10^3\rho$ calculated	= 0.74	0.129	0.070	0.038	0.017	0.0100

This peculiarity can scarcely be explained without the help of the dissociation theory, which, as is seen from the good agreement between the observed and calculated values, agrees very well with experience.

This influence of foreign ions on the degree of dissociation also plays an important rôle in chemical equilibria. Such a one is the equilibrium which takes place on mixing equivalent quantities of two acids and of a base. The stronger acid takes the greater part of the base. According to the theory of Guldberg and Waage the coefficient of partition, the so-called avidity, ought to be proportional to the square root of the relative strengths of the acids, as measured by means of their catalytic action, and Ostwald tried to verify this theorem. But if a strong acid and a weak one compete, the influence of the ions of the salts and of the strong acid diminishes the degree of dissociation of the weak acid in a high degree, whereas the dissociation of the strong acid is nearly undisturbed. The consequence is that the weak acid appears much weaker than according to Guldberg and Waage's theory, which did not consider the dissociation of electrolytes. An exact calculation taught me that the avidity of an acid is not proportional to the square root of its catalytic action, *i. e.*, its degree of dissociation, but very nearly to this action itself, and this theoretical deduction was corroborated by previous experiments by Ostwald as the

following table giving the fractions of the bases (NaOH, KOH and NH_3) taken by the two acids indicates.

	Observed.	Calculated.
Nitric: dichloracetic	0.76 : 0.24	0.69 : 0.31
Hydrochloric: dichloracetic	0.74 : 0.26	0.69 : 0.31
Trichloracetic: dichloracetic	0.71 : 0.29	0.69 : 0.31
Dichloracetic: lactic	0.91 : 0.09	0.95 : 0.05
Trichloracetic: monochloracetic	0.92 : 0.08	0.91 : 0.09
Trichloracetic: formic	0.97 : 0.03	0.92 : 0.08
Formic: lactic	0.54 : 0.46	0.56 : 0.44
Formic: acetic	0.76 : 0.24	0.75 : 0.25
Formic: butyric	0.80 : 0.20	0.79 : 0.21
Formic: isobutyric	0.79 : 0.21	0.79 : 0.21
Formic: propionic	0.81 : 0.19	0.80 : 0.20
Formic: glycolic	0.44 : 0.56(?)	0.53 : 0.47
Acetic: butyric	0.53 : 0.47	0.54 : 0.46
Acetic: isobutyric	0.53 : 0.47	0.54 : 0.46

This is one of the best proofs of the usefulness of the dissociation theory, for any theory which does not suppose that the acid molecules are dissociated, gives calculated figures, which are nearly proportional to the square roots of those given above.

Water is partly electrolytically dissociated. Therefore it reacts with salts, dissolved in it, and hydrolyzes them partially. For salts of a strong acid or base with a weak base or acid the degree of hydrolysis increases nearly proportionally to the square root of the dilution, as was also shown by Shields and others. For salts of weak acids with weak bases the peculiar fact is deduced theoretically that if the dilution is not extremely great, the degree of hydrolysis remains nearly independent of the dilution. This was also found by Walker for anilinacetate, the hydrolysis of which did not increase more than from 54.6 per cent. to 56.9 per cent., when the volume, in which one gram-molecule of anilinacetate was dissolved, increased from 12.5 to 800 liter.

Now Hantzsch drew the conclusion from some of his experiments that salts of aliphatic nitrocompounds and of isonitrosoketones behave abnormally in regard to hydrolysis and supposed, that this circumstance was due to a transformation of the reacting acids or bases into their so-called pseudo-forms. This assertion does not conform to the theory of electrolytic dissociation. A little later also Hantzsch in collaboration with Ley found on closer examination that the isonitrosoketones do not at all disagree in their hydrolytic properties with the dissociation theory. The same was the result of an investigation by Lundén regarding the aliphatic nitro-compounds.

A certain difficulty for the dissociation theory seemed to arise from an investigation of Wakeman regarding the conductivity of weak acids in mixtures of alcohol (up to 50 p. c.) and water. These acids—acetic, cyanacetic, glycolic, monobromacetic and orthonitrobenzoic—obey, in aqueous solution, the law of mass action. Wakeman found that the dissociation constant of the same acids in mixtures of alcohol and water decreases with increasing dilution, which would then be in contradiction to the dissociation theory. The same was also found for cyanacetic acid in a mixture of water and acetone.

The result of Wakeman seemed corroborated by an investigation by Lincoln on the same subject. But nevertheless their observations seem to have suffered from some grave systematic experimental error. Godlewski made very careful measurements on just the same acids as Wakeman and found that these weak acids follow the demands of the dissociation theory in all

mixtures from pure alcohol to water. He found the following dissociation constants multiplied by 10^5 for the following acids (at 18°):

Alcohol, per cent....	0	10	20	30	40	50	60	70	80	90	100
Salicylic acid 10^5k...	100	95	83	57	32	18	11	4.6	1.8	0.57	0.013
Cyanacetic acid 10^5k	370	360	210	192	120	76.5	57.3	29.2	10.7	2.5	0.05
Bromacetic acid 10^5k	138	131	85	58	35	20.5	10.2	5.7	1.7	0.43	0.015

The dissociation constant at first decreases slowly, when alcohol is added, then more rapidly and when the quantity of water is only 70 to 80 per cent., the dissociation constant diminishes quite suddenly on further addition of alcohol. The order of the acids in regard to their strength is not the same in alcoholic as in aqueous solution. The dissociation constants in alcohol are about 10,000 times smaller than in water.

The most violent attack on the modern theories or especially on that of van't Hoff is found in a memoir of Kahlenberg. He determined the osmotic pressure of solutions of cane sugar in pyridine, separated from pure pyridine by a membrane of caoutchouc, which is permeable to pyridine but not to cane sugar. He found that his measurements did not at all agree with the gas laws for solutions. These measurements were repeated by Cohen and Commelin. They found the experiments connected with extremely great difficulties, which had caused very great errors in Kahlenberg's measurements. He was therefore not at all authorized to draw the conclusions, cited above, from them.

The theories of the analogy between the gaseous and the diluted state of matter and of the electrolytic dissociation have been tried with perfect success in so many cases and found to be of such great use as well

for the chemical as for the physical and even the biological sciences, that van't Hoff's words of 1890 regarding the electrolytic dissociation theory that it had become nearly a fact are still more valid now than 20 years ago. The same is of course true for van't Hoff's theory itself which is indissolubly connected with the dissociation theory.

LECTURE X.

THE ABNORMALITY OF STRONG ELECTROLYTES.

THE great difficulty in the application of Guldberg and Waage's law to the equilibria between ions and non-dissociated salts (acids or bases) lies, as has been said above, in the great deviation of the strong electrolytes, which furthermore are of the greatest importance in nature and the industries. A very great number of attempts have been made to explain this deviation, but none of them has to this day been crowned with success, and I therefore give only a short review of them. They may be grouped chiefly under the four following headings:

1. Theories introducing a correction regarding the change of the ionic friction with dilution.

2. Theories introducing a correction for the electric attraction of the charges of the ions.

3. Theories regarding the influence of foreign substances on the osmotic pressure (the so-called salt-action).

4. Theories regarding the binding of water to the ions.

As we have seen above, the friction of the ions is, if not precisely proportional to, yet very closely related to the viscosity of the surrounding solution. Now for all aqueous solutions of salts, except those of NH_4, K, Rb and Cs—amongst those examined—the viscosity increases with the concentration. If we corrected the

conductivity for the viscosity, we would, in the most cases, obtain a by far higher degree of dissociation than that calculated in the usual way and this correction would make the discrepancy still greater than before. The deviation takes place according to an empirical law found by van't Hoff (cf. p. 133), namely, that the dissociation constant in the equation of equilibrium increases nearly proportionally to the square root of the concentration of the ions. After a correction the "constant" would increase still more rapidly with concentration—for very dilute solutions, below 0.1 normal, the correction would be of very small importance. Yet Jahn advocated a theory that the ionic friction increases very markedly with dilution, *e. g.*, by about 13, 10 and 8 per cent. for K, Na and H ions, when they are diluted from 0.0334 normal solution to infinite dilution. Without further explanation, this hypothesis to which we come back a little later, seems inadmissible.

The ions are supposed to move quite freely in the solutions and therefore to exert an osmotic pressure equal to that of an equal number of common molecules, and this hypothesis is in accord with the observations regarding freezing and boiling points of solutions. Now if a positive ion tried to fly out from a solution, *e. g.*, into superposed water it would be held back by the negative charge of the rest of the solution and hence the osmotic pressure would be less than if the ions were wholly free. This diminution of the osmotic pressure would for each ion be the greater the less the distance between the ions, *i. e.*, the greater the concentration was. Now the equation of equilibrium indicates (for salts of two monovalent ions, such as KCl), that

$$o_i^2 : o_n = K$$

where the osmotic pressure of the ions is indicated by o_i, that of the non-dissociated salt with o_n, and K is the constant of dissociation. Now o_i is supposed to be proportional to the concentration c_i of the ions, but according to the electrostatic attraction theory it ought to increase more slowly. If it were proportional to $c_i^{0.75}$, we would find again the rule found by van't Hoff. In reality it increases according to another law and does not fit very well with the experimental determinations. The greatest objection to this theory is, that it would demand a decidedly smaller lowering of the freezing point, especially in not too small concentrations, than that calculated from the determinations of the conductivity. The deviation from the theoretical law is in the opposite direction and increases with concentration. For small concentrations, *e. g.*, up to 0.2 normal for KCl, I have shown that theory agrees with experiment, if the degree of dissociation is calculated as proportional to the molecular conductivity.

The said electrostatic theory has been developed by v. Steinwehr, Liebenow, Malmström and Kjellin.

As early as in 1788 Blagden stated in an excellent investigation that the freezing points of aqueous solutions in general are proportional to the concentration. But in some cases, *e. g.*, for H_2SO_4, K_2CO_3, etc., he observed that the lowering of the freezing increases more rapidly than the law of Blagden indicates. In other cases the increase was less than according to the law. The same was found by Rüdorff in 1861, and stated by De Coppet in 1871, and afterwards by many others. Where the lowerings were less at high concentrations

than according to Blagden's law, this could easily be explained as due to the dissociation which diminishes with increasing concentration. But when the theory of ionization was applied, the more common deviation in opposite direction remained unexplained.

Rüdorff supposed that the said salts, which give a too great lowering of the freezing point in concentrated solutions, bound a certain part of the water as water of hydration, *e. g.*, $CaCl_2$ bound $6H_2O$, so that the whole quantity of water was not used for the dilution. This correction helps only if we consider the concentration as the number of salt-molecules in 100 g. of water or in 100 molecules of water and of salt, and not, as is common, in gram-molecules per liter. The idea of Rüdorff was carried out on a large scale by H. C. Jones and his pupils, with due regard to the dissociation.

From these determinations it was calculated that hydrates were formed with very many molecules of water, *e. g.*, the chlorides and nitrates of bivalent metals with about 18, the corresponding salts of trivalent metals with 24, glycerol with 12, cane sugar and fructose with 6 molecules of water.

Of course the simplest case is that where no dissociation takes place, *i. e.*, with non-electrolytes. These were investigated by Abegg, who found that in many cases these substances give an increasing molecular lowering of the freezing point with increasing concentration; in other cases the deviation from Blagden's law was in the opposite direction.

Some very accurate experiments regarding the osmotic pressure of solutions of cane sugar and glucose were performed by Morse and his collaborators and by

Berkeley and Hartley. They were struck by the nearly strict proportionality between osmotic pressure and concentration if this was taken according to Raoult's directions, *i. e.*, in gram-molecules dissolved in 100 g. of water. But Sackur showed that this strict proportionality occurred only at about 20° C.; at 0° C. it was necessary to suppose a binding of water to the molecules of sugar (as is already seen from Abegg's work). Sackur calculated the osmotic pressure p from the data of observations with the help of a modification:

$$p(v - b) = RT$$

of van der Waals's well-known formula, already used by Noyes. v is the volume and T the absolute temperature of the solution containing 1 gram-molecule, R is the gas-constant (1.985 cal.) and b the so-called covolume. b is just as great as the volume of the dissolved sugar at 23° C. (b = 0.093 for dextrose and 0.20 for cane sugar) but it is greater at 0° (0.16 and 0.31). He found the following values of 1,000 b at 0°.

	Mol. Weight	1,000 b.		Mol. Weight.	1,000 b.
Methylalkohol	32	50	Glycerol	92	106
Ethylalkohol	46	72	Chloral	147.5	125
Acetone	58	55	Dextrose	180	160
Acetamide	59	58	Fructose	180	210
Ethylformate	74	140	Saccharose	342	305
Methylacetate	74	81			

In general b increases with the molecular weight and the lowering of temperature. Difficulties arise because sometimes there is found a deviation from van't Hoff's law even in very dilute solutions (*e. g.*, in Abegg's figures), and Noyes in some cases found negative values of b, especially in non-aqueous solutions.

The question of the formation of hydrates in solutions has been treated in a masterly manner by Washburn in a monograph to which I refer for further information.

A very interesting phenomenon has been discovered by Svedberg. He investigated the validity of the gas laws for suspensions of gold or mercury (particles of 58.10^{-6} and 142.10^{-6} mm. diameter respectively) and arrived at the peculiar result that these suspensions in extreme dilutions ($3{,}700.10^6$ and $1{,}500.10^6$ particles, respectively, per cubic centimeter) obey the law of Boyle, but that in 10 and 15 times respectively greater concentrations their osmotic pressures are about 1.5 and 2 times respectively greater than theory demands. Here there is no question of the impossibility of explaining these deviations by supposing the formation of hydrates, the quantity of water bound to the few particles of metal would under all circumstances be absolutely insignificant.

Tammann measured the osmotic pressure of cane sugar solutions to which he had added 0.91 mol. normal solution of copper sulphate. This solution was on the outside of the cell; in its interior was a solution of $K_4C_6N_6Fe$. He found the osmotic pressure of the sugar to be 1.30 to 1.58 times greater than the theoretical value (for solutions containing 0.04 to 0.06 gram-molecule per liter). Hence the osmotic pressure of the cane sugar was increased by an average of 40 per cent. through the presence of the copper sulphate. Experiments on the freezing point of similar solutions and those containing no copper sulphate gave similar results. The same was the case with solutions of isobutyl alcohol in the presence of $CuSO_4$.

Other experiments were performed by Abegg, who measured the osmotic pressure by the aid of diffusion with the same results as Tammann. He found that salts (NH_4NO_3 and NH_4Cl) diffuse from an aqueous solution which contains a little quantity of alcohol (2 normal) into an aqueous solution equally concentrated in regard to the salts, without alcohol. The presence of the alcohol was therefore found to increase the osmotic pressure of the salt.—Evidently this is the same phenomenon as that termed salting out of substances from water.

Quite recently Rivett has examined this peculiarity. He investigated solutions containing salts and cane sugar and found that if the described increase in the lowering of the freezing point is attributed to the increase of the osmotic pressure of the cane sugar this increase is proportional to the product of the quantity of the salt and that of sugar present. The least influence was produced by barium nitrate which in 0.5 equivalent normal solution increased the osmotic pressure of the sugar by only 4 per cent., the greatest by lithium chloride which in 0.5 equivalent normal solution gave an increase of 30.5 per cent. Similar experiments were made with ethyl acetate with similar results (changing between 10 per cent. for barium nitrate and 30 per cent. for sodium chloride in 0.5 equivalent normal solution).

Further experiments are necessary for ascertaining if an increase in the osmotic pressure of the salt or of the cane sugar, respectively, or of the ethyl acetate or both (which is probable) has taken place.

These experiments remind very much of the influence

of salts on the velocity of reaction of acids acting upon cane sugar or ethyl acetate. This velocity is increased to a high degree, about 30 per cent. on adding a 0.5 equivalent normal chloride or nitrate (for inversion of cane sugar) whereas an addition of methyl or ethyl alcohol or even of a weakly dissociated electrolyte such as acetic acid or chloride of mercury has no, or only a very small, influence. For the action of salt on the saponification of ethyl acetate by means of acids the effect is less, about 12 per cent. for 0.5 *n* chlorides and only 4 per cent. for 0.5 *n* nitrates. In saponification by means of bases the action is very small and different in different cases, sometimes negative. The action is proportional to the concentration of the salt.

Moreover, the dissociation of weak acids is increased by the addition of neutral salts, which indicates an increase in the osmotic pressure of the non-dissociated part of the acid by the presence of the salt.

The solubility of different substances such as gases, *e. g.*, H_2, O_2, CO, N_2, NO, or organic substances, *e. g.*, ethyl acetate and phenylthiocarbamide, in water is diminished by the addition of salts but not of non-dissociated substances, which may be explained as due to an increase of the osmotic pressure of those substances by the presence of these salts. Washburn has given a review of this action.

All these phenomena indicate that the osmotic pressure of a substance is in a high degree dependent on the presence of foreign substances especially of salts in the solvent water. Attempts have been made to explain this action through the binding of water to the salts, but the success attained has been very moderate. On the other

hand it is clear that if the ions act so as to increase the osmotic pressure of non-dissociated substances, the dissociation constant of salts may be increased by the presence of its own ions, *i. e.*, by its own concentration, which explanation I proposed in 1899. This hypothesis has been taken up by Partington. He concludes, from the great ionizing influence of free ions in gases, that there exists a similar influence of free ions in liquids and shows that a formula deduced from the ionization of salts from this idea agrees well with experience.

Of course there is no doubt that electrolytes in solution bind water. Jones showed that in solutions containing sulphuric acid and water dissolved in acetic acid, molecules of the composition $H_2SO_4 + H_2O$, $H_2SO_4 + 2H_2O$ and probably $H_2SO_4 + 3H_2O$, exist, which are yet dissociated in a high degree. Heydweiller, who investigated the specific weight of different solutions of salts in water, expressed his results by the formula:

$$\Delta_s = A_s i + B_s (1 - i),$$

where i is the number of ions (in gram ions) and $(1 - i)$ is the number of undissociated molecules in one gram-molecule. Δ_s is the change of density through the addition of the salt, divided by its concentration. A_s is evidently a constant from which the density of the ions and B_s one from which the density of the undissociated molecules may be calculated. This latter density was found sometimes to agree with that of anhydrous salts not only for salts which do not crystallize with water, *e. g.*, for KNO_3, $KClO_3$, $AgNO_3$, but also for salts which bind water strongly such as

LiCl, CaI_2, etc. In other cases it agreed with the density of known hydrates such as $Na_2SO_4 + 10H_2O$, $NaBr + 2H_2O$, $CaCl_2 + 6H_2O$, $MgCl_2 + 6H_2O$, $CuSO_4 + 5H_2O$, $BaCl_2 + 2H_2O$, $MgSO_4 + 7H_2O$, etc. In some cases the hydrates indicated in this manner seem to contain more water than the solid salt hydrates which are stable at the same temperature, but generally the inverse is true. We may therefore say that the non-dissociated parts of dissolved salts are hydrated to about the same degree as the salt in the solid state at the same temperature (under normal conditions).

The constant A_s gives the density of the ions. Of course there are always two ions present, one positive and one negative, and A_s is therefore of a strictly additive nature. As these "density modules" of the ions are of a high practical value also, I reproduce them here (for equivalent weights):

Positive ion:	H	NH_4	Li	Na	K	Rb	Cs	Ag
Density module	−1.25	−0.94	−0.31	+1.35	2.16	6.52	10.59	9.70
Positive ion:	½Mg	½Ca	½Sr	½Cu	½Zn	½Cd	½Ba	½Pb
Density module:	1.36	2.04	4.38	4.06	4.67	5.48	6.53	10.37
Negative ion:	OH	CNS	$C_2H_3O_2$		F	Cl	Br	I
Density module:	3.37	2.88	3.14		3.08	3.01	6.67	10.31
Negative ion:	NO_3	ClO_3		IO_3	½CO_3	½SO_4	½CrO_4	
Density module:	4.56	5.78		16.04	4.92	5.51	6.53	

A_s, the sum of the two modules of a salt's ions, is always greater than B_s, the corresponding quantity of the undissociated salt. Therefore we conclude that ionization is combined with a contraction of volume. This is also well known in other cases. For instance if a base is neutralized with an acid, both in highly diluted solutions, the whole action consists, as has been said above, in a combination of the hydrogen ions of

the acid with the hydroxyl ions of the base. The accompanying expansion Δv is dependent on temperature t in a rather complicated manner as is indicated by the table

t	0	10	20	30	100	110	120	130	140	°C.
Δv	20.9	20.1	19.2	18.7	18.7	20.0	22.5	25.4	25.7	c.c.

The peculiar behavior that a minimum occurs between 30° and 100° depends upon the occurrence at low temperature in the water of so-called ice molecules together with the real water-molecules. The ice-molecules have a greater volume than the water molecules, therefore the volume of neutralization is greater at 0° than at 30°. Otherwise the neutralization volume Δv would without a doubt increase continually with increasing temperature. These figures are found for the neutralization of NaOH with HCl. Ostwald investigated the neutralization of different strong acids with KOH and NaOH and found the following neutralization volumes:

Acid	HNO_3	HCl	HBr	HI		
Δv for KOH	20.0	19.5	19.6	19.8	average	19.7
Δv for NaOH	19.8	19.2	19.3	19.5	"	19.5

There is still a little difference between the figure for KOH and NaOH. If it is real or depends upon experimental errors is difficult to decide.

In the neutralization of weak acids Ostwald found a much lower Δv. This depends upon the almost wholly undissociated state of these acids. The expansion on neutralization is here equal to the difference between the expansion due to the combination of the two ions OH and H to form water and that, which occurs when the weak acid is formed from its ions.

Now this latter may be determined from the change of the electrolytic dissociation with change of pressure. Fanjung therefore determined the conductivity of weak acids under high pressures, up to 500 atm., and therefrom calculated the volume of dissociation of these acids, and by subtracting that from the neutralization volume of strong acids with KOH or NaOH he calculated the neutralization volume of the weak acids and compared his results with those found directly by Ostwald. His results are reproduced below:

Substance.	Volume of Neutralization. Obs. (Ostwald).	Calc. (Fanjung).
Formic acid	7.7 c.c.	8.7
Acetic acid	10.5	10.6
Propionic acid	12.2	12.4
Butyric acid	13.1	13.4
Isobutyric acid	13.8	13.3
Lactic acid	11.8	12.1
Succinic acid	11.8	11.2
Maleic acid	11.4	10.3

The agreement is as good as might be expected considering the difficulty of the experiments.

Ostwald also determined the neutralization volume of ammonia with strong acids and found it to be 26 c.c. at 15° C. This observation indicates that in the electrolytic dissociation of ammonia an expansion of 6.4 c.c occurs, which seems at first not to be in accord with the general fact that dissociation is followed by contraction. But we remember that at 15° C. ammonia consists of 59.4 per cent. of NH_3 and 40.6 per cent. of NH_4OH (cfr. page 155). The dissociation process may here be regarded as consisting of two combined processes, the formation of NH_4OH from the 59.4 per cent. NH_3 and a corresponding quantity of water and then

the dissociation of NH_4OH into NH_4 and OH. This latter process may be accompanied by a contraction if the first process causes an expansion of more than 6.4 c.c.

It seems peculiar that dissociation is accompanied by contraction, although such examples are known—the simplest is perhaps that ice has a greater volume, but probably more complex molecules, than liquid water, or that a contraction occurs on mixing ethyl alcohol and water. Drude and Nernst gave the following explanation. The free energy of a charged particle, such as an ion, is the less the greater the constant of dielectricity in its surroundings. The dielectric constant of water is very high and increases with its compression. Now the free energy tends to a minimum, therefore the water has a tendency to contract in the neighborhood of the ions. This contraction is sometimes so great that the volume of the solution is less than that of the water contained in it. Such a contraction on ionization has also been observed by Carrara and Levi on dissolving electrolytes in methyl or ethyl alcohol or urethane, and by Walden on dissolving iodide of tetraethylammonium in different solvents. In this latter case it was always nearly the same, namely 13 c.c.

Another explanation of this fact has been given, namely that the ions may bind water and this binding might well cause a strong contraction. This idea that the ions bind water might be elucidated by studying the relative conductivity of the ions and especially if the ions carry water with them in electrolytic experiments. Kohlrausch had through the close coincidence of the temperature variation of fluidity and electric

conductivity of salt solutions been led to the hypothesis that the ions are surrounded by an "aqueous atmosphere." The idea was developed by Bousfield who applied Stokes' law to the mobility of ions in their solutions. The friction of a little sphere against the surrounding medium is proportional to the viscosity of that medium and the radius of the moving sphere.

Now the atomic volume of Li, Na, K, Rb and Cs increases from the first to the last. We might therefore suppose that Li should move more easily than Na and that more easily than K in a very dilute solution, the viscosity of which may be considered equal to that of water. In reality this is the order of the rate of diffusion of these metals (9.5 for Li, 7.3 for Na, 4.9 for K, 4.7 for Rb and 4.6 for Cs) in mercury, but the order of the mobility of the corresponding ions in aqueous solutions is the inverse, which peculiar circumstance has ever attracted attention as being difficult to understand. Bousfield calculated the radii of different ions, which according to Stokes' law ought to be characteristic of them in order that they should possess the conductivity really observed. I give below a reproduction of Bousfield's table, in which l_{18} is the conductivity of the ion in question at 18° C. and r its radius at three different temperatures, namely -2, $+18$ and $+38$° C., that of the hydrogen ion at 18° C. taken as unity. α is the temperature coefficient of l at 18°. For a comparison I have introduced into the table under the headings l_k and $\alpha_k 10^3$ the values of the conductibilities of the ions and their temperature coefficients multiplied by 10^4 at 18° according to Kohlrausch (Praktische Physik., 11th ed., 1910).

Kohlrausch has given some other figures regarding these magnitudes, which I also give here because of their great usefulness. They are:

Ion.	Cs	Tl	½Ca	½Cd	½Ra	Br	SCN	BrO_3
l_k	68	66	51	46	58	67	56.6	46
$\alpha_k.10^4$	212	215	247	245	239	215	221	—

Ion.	IO_4	ClO_4	CHO_2	$C_2H_3O_2$	$\frac{1}{2}CrO_4$	$\frac{1}{2}C_2O_4$
l_k	48	64	47	31	72	63
$\alpha_k.10^4$	—	—	—	—	—	231

Ion.	l_{18}.	$\alpha.10^4$.	r at −2.	r at +18.	r at +38.	l_k.	$\alpha_k.10^4$.
H	318	154	0.801	1.000	1.196	315	154
OH	174	179	1.541	1.828	2.078	174	180
NO_3	61.8	203	4.57	5.145	5.59	61.7	205
I	66.4	206	4.28	4.79	5.17	66.5	213
ClO_3	57	207	4.99	5.58	6.01	55	215
Cl	65.4	215	4.41	4.86	5.16	65.5	216
Rb	67.9	217	4.29	4.68	4.96	67.5	214
K	74.6	220	4.53	4.91	5.17	64.6	217
NH_4	63.7	223	4.64	4.99	5.23	64	222
$\frac{1}{2}SO_4$	69	226	4.31	4.61	4.80	68.4	227
Ag	54.7	231	5.50	5.81	6.00	54.3	229
½ Sr	53	231	5.68	6.00	6.19	51.7	247
F	45.5	232	6.63	6.99	7.20	46.6	238
IO_3	33.9	233	8.91	9.38	9.65	33.9	234
$C_2H_3O_2$	34	236	8.95	9.35	9.58	35	238
½ Ba	57	239	5.38	5.58	5.68	55.5	239
½ Cu	49	240	6.27	6.49	6.60	46	—
½ Pb	61.5	244	5.05	5.17	5.22	61	240
Na	43.5	245	7.15	7.31	7.37	43.5	244
½ Mg	46.0	255	6.93	6.91	6.84	45	256
½ Zn	46	256	7.00	6.91	6.82	46	254
Li	33.4	261	9.68	9.52	9.33	33.4	265
½ CO_3	70	269	4.72	4.54	4.39		

The temperature coefficient of the fluidity of water at 18° is 251.10^{-4}, therefore r increases with temperature for those ions which have a smaller α, decreases for ions with $\alpha > 251.10^{-4}$. The table is therefore arranged according to the magnitude of α. A great difficulty at first arises in supposing that the radii of the ions

increase with temperature in such a high degree as indicated above (the cubic temperature coefficient of expansion of fluids seldom reaches 0.001 and the linear coefficient of expansion is only a third of that magnitude). It is therefore, according to Bousfield's hypothesis, necessary to suppose that the ions bind more and more water the higher the temperature rises. As an example we cite the estimate of Bousfield that one molecule of NaOH at 0° attaches 19.9, at 20° 22 and at 40° 25.7 molecules of H_2O. This conclusion does not at all agree with our experience regarding the hydration of solid salts, which always decreases with rising temperature,* nor is it in accordance with the electrostriction theory for the dielectric constant of water decreases rapidly with increasing temperature. The Li-ion with its aqueous envelope ought to be eight times as great as that of the Rb-ion or the Cs-ion ($l_{18} = 68$); it ought then to bind a very great number of water molecules. The K-ion, which seldom enters into solid salts with crystal water, ought to bind a rather great number of water molecules in order that the complex should get a greater radius than the Rb- or Cs-ion. (The atomic volume of these metals in the solid state is for Li 13.1, for Na 23.7, for K 45.5, for Rb 56, and for Cs 71 cubic centimeters.) In the same manner the F-ion has a greater volume than the Cl-ion and this exceeds the I-ion. Otherwise the ions possess in general the less mobility the more composite they are, as Ostwald at first showed for ions of organic acids, and Bredig for the corresponding ions of bases.

* An exception from this law has been related by Koppel for sulphate of cerium (Zeitschrift für anorganische Chemie, *41*, 377 (1904)). It is well worth a reinvestigation.

The work of Bousfield leaves us in ignorance of the precise quantity of water which is attached to each ion, it only indicates that it ought to be very great. This want has been removed by the more recent work of Buchboeck, Washburn and Riesenfeld and Reinhold.

It is possible to decide if water is dragged with the ions if they wander in a non-aqueous medium which is diluted by addition of water. The main parts of the liquid are not altered but in the neighborhood of the electrodes the transported water is deposited and may be determined according to the method of Hittorf. Nernst, Garrard and Oppermann were the first to use this method. They dissolved boric acid in the solutions to be examined, and determined if the concentration of the boric acid changed during the passage of the current. The analytical method used was not exact enough to allow evident conclusions. The same was the case with some later investigators in this field until Buchboeck took up the problem. He used mannite and resorcine as indicators. He electrolyzed hydrochloric acid, which after the experiment was removed from a sample of a given volume by means of silver carbonate and consequent treatment with sulphureted hydrogen to remove traces of silver, after which the mannite or resorcine present was determined by evaporating and weighing. Washburn used arsenious acid, raffinose or saccharose as indicators and determined the concentration of these latter simply by measuring the rotatory power of the solution before and after the electrolysis.

Of course it is necessary to know that the indicator is not carried forward by the current in the same

manner as colloids. Indeed there are some experiments by Coehn which seem to indicate such a transport of cane sugar and probably raffinose behaves in the same manner. In all cases Washburn stated that with his experimental arrangements no such effect could be observed. The indicators should also not unite with the dissolved salts and enter into complex ions, nor enter into reaction with substances deposited at the electrodes through the electrolysis. For this latter purpose unpolarizable electrodes of silver with a coating of silver chloride were used and the electrolytes were chlorides (of H, Li, Na and K). The concentration of the indicator always increased in the neighborhood of the anode, whereby a transport of water in the direction of the current is indicated.

The effect is a differential one. If the two ions migrate with the same velocity and carry each the same number of water molecules, then the concentration of the water will not change. Therefore we must make a hypothesis regarding the number of water molecules transported by the one ion in order to determine the number of water molecules transported. If it is supposed that the chlorine-ion does not carry any water, Washburn's figures give the following values for the positive ions:

$$H + 0.28\ H_2O,\ K + 1.3\ H_2O,\ Na + 2.0\ H_2O,\ Li + 4.7\ H_2O.$$

If we suppose that Cl carries one molecule of water, we must, as is easily seen, add to the 0.28 molecule of water combined with the H-ion, as calculated above, a quantity inversely proportional to the relative veloc-

ity, *i. e.*, in this case 65.5 : 315 = 0.2 (cfr. p. 134, Washburn gives the ratio 0.185). The corresponding figures for K, Na and Li are according to Washburn 1.02, 1.61 and 2.29. Thus for instance if we suppose that the chlorine-ion carries six molecules of water, then the Li-ion carries 4.7 + 6.2.29 = 18.5.

It is clear that this transportation of water has influenced the concentration of the solutions in which Hittorf and his successors determined the migration of ions. At extreme dilution this difficulty disappears, for then the change of the relative concentration of the water through its transportation becomes inappreciable. Now there has been worked out by Denison and Steele a new method for directly measuring the velocity with which the ions proceed by means of optical reactions which they cause. These investigators, for instance, passed a current through three solutions of LiCl, KCl and KCH_3CO_2, so that the slower ion Li or $C_2H_3O_2$ followed the more rapidly moving ion K or Cl respectively in the direction of their movement. Then no mixing of the solutions occurred and their boundary surfaces remained sharp and could be determined by a telescope through the change of the refractive indices in them. These boundary surfaces move with the same velocity as the ions K and Cl in the middle portion of the conducting solution. This method is independent of the concomitant transportation of water.

From his own experiments Washburn determined the ratio of migration of the positive ion according to the chemical method used by Hittorf, then corrected it with regard to the transportation of the water and

compared it with the results of Denison and Steele. He found for 1.25 normal solutions of KCl and NaCl at 25° the following values:

	Hittorf's Method.	Corrected.	Denison-Steele's Method.
KCl	0.482	0.495	0.492
NaCl	0.366	0.383	0.386

The figures of Denison and Steele are properly valid for 1 n solutions at 18°, but the difference between these solutions and 1.25 n at 25° is in this regard insignificant.

This confirmation of the correctness of Washburn's views and determinations seems very valuable, otherwise one would not have been quite certain that a part of the sugar or raffinose or arsenious acid had not wandered also, as negative ion-compounds of alkaline salts with sugar are well known, and may, to a small extent, exist in aqueous solution.

Even Washburn could not with the means at his disposal decide how great a quantity of water is attached to the ions, but only that Li carries more water than Na, Na than K and K than H, and that there is certainly a transportation of water with the ions. The order of the ions Li, Na and K is the same as that of their solid salts in regard to their capacity for binding water.

A new step was taken by Riesenfeld and Reinhold. They combined the methods of Washburn and Bousfield. If in a salt ak composed of the anion a and the cation k, these two ions contribute to the conductivity with the fractions w_a and $(1 - w_a)$ and if the anion carries A molecules and the cation K molecules of water, then the number x of water molecules transported

to the anode, accessible to analysis after the passage of 96,550 coulombs is as is easily seen:

$$w_a A - (1 - w_a) K = x.$$

From the change of the migration rate n_a, as determined by Hittorf, with concentration it is possible to determine x, as Washburn pointed out, for

$$n_a = w_a + x/a,$$

if 1 equivalent of salt is dissolved in a molecules of

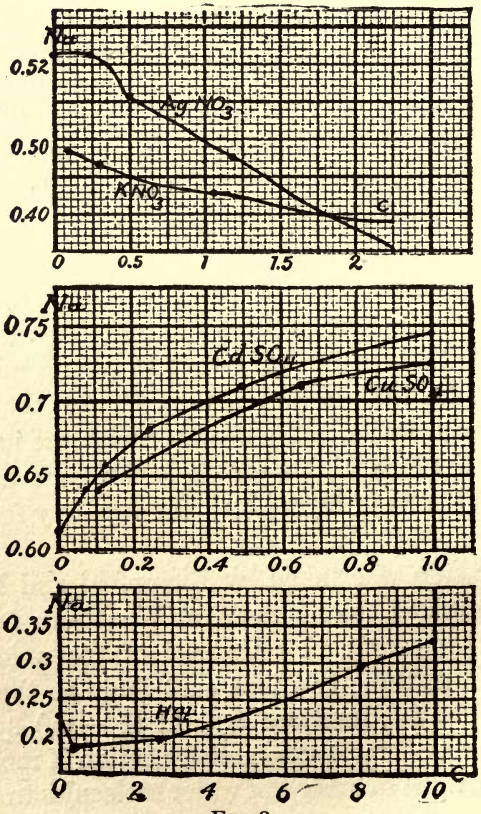

FIG. 3.

water. In the accompanying diagrams the variation of n_a with concentration ($c = 55.5/a$ for dilute solutions) is represented.

Further, Riesenfeld and Reinhold supposed that the number of water molecules combined with an ion is so great—as we have seen Bousfield's figures indicate that this number is generally very high—that the volume of the ion with accompanying water is proportional to this number. In this case the velocities of the ions are inversely proportional to the radii of these volumes, *i. e.*, to the cube root of the accompanying number of water molecules A and K. Hence as x is known we have two equations for determining A and K, and we may calculate both of them. Riesenfeld and Reinhold now calculated the number of water-molecules attached to the 8 ions entering into the electrolytes HCl, KNO_3, $AgNO_3$, $CdSO_4$ and $CuSO_4$, for which x is relatively well determined. From these figures they calculated seven values for the number of H_2O molecules bound to the ion Cl by comparing its conductivity with those of the seven other ions. They found values varying between 16 and 24 with an average value of 21. With the aid of this value and the known conductivities of the ions they found the following numbers of water molecules accompanying each ion:

Ion:	H	K	Ag	½Cd	½Cu	Na	Li
Number of H_2O-molecules:	0.2	22	37	55	56	71	158
Ion:	OH	½SO_4	Br	I	Cl	NO_3	ClO_3
Number of H_2O-molecules:	11	18	20	20	21	25	35

It is of course impossible to suppose that a lithium-ion is chemically bound to 158 molecules of water. It is perhaps bound to one, two or three molecules of water

as the solid salts $LiCl + H_2O$, $LiBr + 2H_2O$ and $LiI + 3H_2O$, or if we reserve one H_2O for the anion, the Li-ion may be bound to about $2H_2O$. It is probable that in the solution there occur Li-ions bound to 1 to 3 molecules of water. The motion of a complex molecule $H_2O - Li - H_2O$ may be estimated to cause about double the effort of dragging Li alone. Therefore the mobility of Li is only about one half of that of Cs, which moves the most rapidly of all monovalent ions. In this case we except the ions H and OH of the water HOH itself on grounds cited above (cf. p. 134). The friction of the Na-ion $1/43.5 = 0.023$ lies about midway between that of Li ($1/33.4 = 0.03$) and that of Cs ($1/68 = 0.0147$). Hence we conclude that the Na-ions are on an average bound to about one molecule of water. The other monovalent ions are bound to greater or less quantities of water, which as averages generally are fractions lying between zero and about two. With rising temperature the number of water molecules bound to the ions dissociate off; they then approach the limit value, which is characteristic for ions without "ionic water." Therefore the molecular conductivity of different monovalent ions converge towards a common value with rising temperature. The bivalent ions ought to converge to double this value, as Noyes has also stated for SO_4.

Now Washburn has found that Li drags with it about 5 molecules of water which at first seems to conflict with the assertion that on an average Li has only two molecules of "ionic water." But as is well known from the doctrine of the fluidity a small particle moving in water carries with itself a rather thick "water envelope."

The molecules of water, with which the moving particle collides, also get a pull in the direction of the moving particle and are carried with it. Evidently the number of water molecules dragged in this manner increases with the complexity of the ion and therefore also with the number of ionic water molecules.

That only a very small number of water molecules is bound to the ions is evident from their very marked individuality in moving through the water, especially if we consider the influence of the temperature on the mobility. The number of water molecules dragged with the ions may of course be considerably greater.

An inspection of the values given by Bredig regarding conductivities of organic ions consisting of a great number of atoms, shows that their conductivities are roughly inversely proportional to the third root of the number of atoms contained in the molecule. This behavior corresponds to the law of Stokes.

The hydration of a dissolved substance increases with dilution. Therefore we should also suppose that the average number of ionic water molecules increases with dilution. The conductivity of the ions decreases very rapidly with the increasing number of ionic water molecules. Therefore the degree of dissociation calculated from the conductivity does not change so rapidly with dilution as we might expect if we did not consider the diminished mobility at high dilutions. The idea of Jahn (cfr. p. 173) may therefore be considered right, if it is combined with the idea of hydration which is undoubtedly right. I regard this change of mobility and the salt effect as the chief factors which disturb the validity of Guldberg and Waage's law in its application to strong electrolytes.

LECTURE XI.

THE DOCTRINE OF ENERGY IN REGARD TO SOLUTIONS.

THE free energy of a dissolved substance is according to van't Hoff's law just as great as the free energy of the same quantity of matter in gaseous form per gram-molecule, *i. e.*,

$$A = RT \log_e p - RT \log_e p_a \qquad (1)$$

where R is the gas constant 1.985 cal., T the absolute temperature and p the osmotic pressure. This formula indicates the work done in compressing one gram-molecule of a gas from the pressure p_a to the pressure p. If p_a is put equal to 1 then $\log_e p_a = 0$ and

$$A = RT \log_e p \qquad (1a)$$

According to the definition of free energy, A is therefore in this case the free energy of the said mass of gas, if the free energy of the same mass of gas at normal pressure, *e. g.*, one millim. mercury is taken as zero, from which the free energy is counted.

If we have to calculate the change of free energy on evaporating a liquid, we consider that the work done in lifting a piston of cross-section s cm. square, loaded with p kilograms per cm. square, *i. e.*, with a total load of ps kilograms, through a height h is

$$psh = pv$$

where v is the volume passed through by the piston.

If we allow the vapor to lift the said piston, the volume v is filled with saturated vapor. If the evaporated quantity is one gram-molecule, the work done is:

$$pv = RT.$$

By this quantity the free energy of the said unit quantity of liquid exceeds that of the same quantity of vapor, *i. e.*, gas.

A similar calculation may be made regarding a solid or liquid substance and its solution in, *e. g.*, water, in which case the work may be done by lifting a piston, loaded per cm.^{2} with a weight equal to the osmotic pressure of the saturated solution, permeable to the solvent (water), but not to the dissolved body, and separating a saturated solution over this body from a layer of pure solvent.

Of course all these deductions regarding the free energy A are based upon the assumption that we deal with such small concentrations that the laws for ideal gases are valid.

Similar expressions referring to the pressure are used for gas-reactions because they generally take place at constant pressure and because the pressure is generally the quantity observed. The same expression should be used for solutions if their condition was characterized by their osmotic pressure. But the osmotic pressure is very difficult to measure and instead of that we use the concentration c in defining the state of solutions. We therefore transform the equation given above by introducing in the expression of A the formula of Boyle-Gay-Lussac:

$$p = cRT. \qquad (2)$$

We now reckon the free energy from a certain concen-

tration c_a, which is connected to p_a through the equation:

$$p_a = c_a RT. \qquad (2a)$$

Introducing the said values of p and p_a into equation (1) we find:

$$A = RT(\log_e c - \log_e c_a). \qquad (3)$$

If we put c_a equal to the unit of concentration—usually one gram-molecule per liter, we get:

$$A = RT \log_e c. \qquad (3a)$$

Let us consider an equilibrium between a weak acid, which obeys the law of Guldberg and Waage, and its two ions. If their concentrations are c_1 and c_2, then the so-called dissociation constant is $K = c_2^2/c_1$. We wish to calculate the work done in the electrolytic dissociation of one gram-molecule of the acid of unit concentration into its two ions also of unit concentration. For this calculation we make use of the circumstance that an equilibrium exists if the concentration of the acid is c_1 and that of each of its two ions c_2. In other words no work is done if we transform a certain quantity of the acid of the concentration c_1 into its ions when their concentration is c_2 or *vice versa*. Then the work to be calculated consists of three parts: (1) The work done in the dilution of one gram-molecule of the acid from the concentration 1 to the concentration c_1

$$A_1 = RT(\log_e 1 - \log_e c_1).$$

(2) The work done in transforming the said mass of the acid of the concentration c_1 into solutions of its two ions, each of the concentration c_2 at constant volume. This work is zero. (3) The work of condensing

the two solutions of the ions from the concentration c_2 to the concentration 1 (the original volume). This work is

$$A_3 = 2RT(\log_e c_2 - \log_e 1).$$

The total work done is:

$$A = A_1 + A_3 = RT(2\log_e c_2 - \log_e c_1) = RT\log_e K. \quad (4)$$

As K is generally a very small fraction, A is generally negative, *i. e.*, the ions possess in normal solution an excess of free energy above that of the acid in normal solution. If we have an acid in double the normal solution and it is dissociated into its ions to the extent of 50 per cent.—this condition is nearly realized for trichloracetic acid at 25°—then the free energy is zero, for an equilibrium exists between the undissociated acid and its two ions, all three in normal concentration, so that no work is necessary for carrying the process in the one or the other direction. In this case the dissociation constant is 1. The expression above is due to van't Hoff.

Evidently it is very easy to calculate A, if we know K, and van't Hoff did that with the help of the determinations of Ostwald. He found for instance at 25° C. for acetic acid $A = -3{,}240$, for formic acid $A = -2{,}510$, for propionic acid $A = -3{,}320$, for trichloracetic $A = +60$, etc.

The free energy or affinity A is bound to the quantity of heat U developed in a reaction by the following equation, which is easily deduced from the second law of thermodynamics:

$$U = A - T\frac{dA}{dT} = -RT^2\frac{d\log_e K}{dT}. \quad (5)$$

If we know A, or K at a given temperature and U for all temperatures, then we may calculate K for any temperature from the last equation, which was given by van't Hoff. But we know A at absolute zero, for there according to the last equation $U = A$. Then knowing U we may determine A.

If we develop A in a series in the neighborhood of 0° absolute, we get

$$A_t = A_o + BT + CT^2 + \ldots.$$

We need only two terms of T if we do not consider temperatures too far from 0° absolute. Using the last equation we find the following expression for U:

$$U_t = A_o - CT^2; \; U_o = A_o.$$

This equation states that $(dU : dT)$ at 0° absolute is absolute zero, *i. e.*, U does not change with temperature in the neighborhood of absolute zero. This seems to be nearly true. Einstein has recently given a theory according to which the specific heats of substances vanish at absolute zero, therefore also the so-called molecular heat, *i. e.*, the product of the specific heat by the molecular weight is zero. This theory has lately been in a high degree confirmed by the measurements of Schimpff and Pollitzer. Now the change of U with temperature depends on the difference of the molecular heats of the reacting substances on the two sides of the sign of equality in the chemical equation expressing the reaction. If now the molecular heats are zero, then it follows that their differences will also be zero.

The determinations of Schimpff and Pollitzer were carried out only with solid substances. The said regu-

larity is certainly only to be regarded as a first approximation for systems in which gases or solutions enter.

A has a maximum (or minimum) when

$$dA/dt = 0 \therefore B + 2CT = 0,$$

i. e., at an absolute temperature T, which is

$$T = -B/2C.$$

As we shall see this temperature is positive, *i. e.*, occurs, because B and C have (in the cases examined below) opposite signs (cfr. fig. 5, p. 212).

At the same temperature A_t and U_t are equal, for if I put

$$A_t = A_o + BT + CT^2 = U_t = A_o - CT^2,$$

I find

$$BT = -2CT^2, \text{ i. e., } T = -B/2C.$$

At this point we also find:

$$dU/dt = -2CT = B,$$

i. e., the tangent to the U-curve at this remarkable point is parallel to the tangent of the A-curve at the point zero. The A- and U-curves cut each other at two points, at $T = 0$ and at $T = -B/2C$. In the temperature interval between these two points they do not separate much from each other, but from there they diverge more and more rapidly the higher the temperature rises according to the prevalence of the term CT^2 in A above BT. In U the term $-CT^2$ determines the variation, which goes in the opposite direction to that of A.

Other interesting points are those in which A_t and $U_t = 0$. For $U_t = 0$ we have

$$A_o - CT^2 = 0 \therefore T_u = \sqrt{A_o/C}$$

and for $A_t = 0$, we find

$$A_o + BT + CT^2 = 0 \therefore T_a = -B/2C \pm \sqrt{\frac{B^2 - 4A_oC}{4C^2}}.$$

The examples of solutions given below give a positive value of T_a because A_o and C are of the same sign. A does not reach zero for weak electrolytes, for which it may be calculated with sufficient accuracy. In order to elucidate these important theorems, I have calculated the free energy of two solutions, one practically not dissociated, namely of boric acid, and the other dissociated to a high degree. The figures are taken from the tables of Landolt-Börnstein, third edition, t is temperature in °C., T absolute temperature, c concentration (gram mol. in 1000 gm. H_2O).

Boric Acid, $H_3O_3B = 62$.

$A = -7519 + 34.02T - 0.025T^2$.

t	T	$c:2$	$\log c:2$	A obs.	A calc.	Diff.	dA/dt	U
0	273	0.1562	−0.8064	− 86	− 94	+ 8	—	−5656
20	293	0.3164	−0.4997	+ 318	+ 301	+17	20.2	−5372
40	313	0.5523	−0.2579	+ 686	+ 680	+ 6	18.4	−5071
60	333	0.8352	−0.0679	+1019	+1037	−18	16.7	−4778
80	353	1.288	0.1101	+1368	+1376	− 8	17.4	−4404
100	373	2.062	0.3144	+1793	+1794	− 1	16.2	−4041

dA/dt is nearly constant and decreases a little with increasing temperature. Thereby C receives a negative sign, and consequently in this case B a positive one. A_o is negative. These signs of A_o, B and C are, as we shall see later, those generally found. Where A_o, B and C do not come out with these signs we may suspect that the observations are affected by some rather great errors (or the temperature interval is insufficient for determining A_o, B and C with accuracy). As $U = A_o - CT^2$, the numerical value of U decreases

with rising temperature. That B is positive depends upon the fact that the solubility always increases at low temperatures. The solubility is, according to the negative sign of A_o, as we shall see below always vanishing in the neighborhood of absolute zero. The change of A and U with temperature is given for H_3O_3B, $Ca(OH)_2$ and $(C_2H_5)_2O$ in the accompanying diagram.

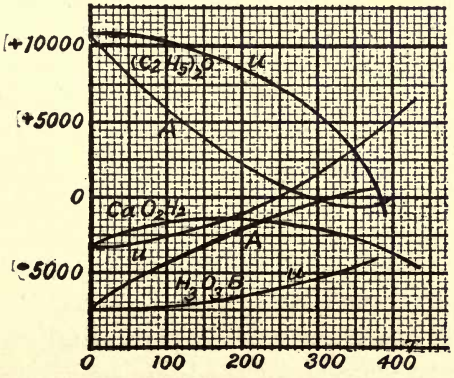

FIG. 4.

We now take a very interesting example, in which U is positive at common temperature, *i. e.*, in which heat is developed on solution, namely the solubility of $Ca(OH)_2$.

CALCIUM HYDRATE $Ca(OH)_2 = 74$.

t	T	c	log c	W obs.	W calc.	Diff.	dW/dt	U	U. 2.62
0	273	0.0234	0.3691–2	−1910	−1885	−25	—	+ 627	+ 1643
40	313	0.01856	0.2688–2	−2331	−2332	+ 1	− 9.6	+1799	+ 4714
80	353	0.01196	0.0779–2	−2938	−2942	+ 4	−14.3	+3130	+ 8200
150	423	0.00446	0.6497–3	−4356	−4380	+24	−19.1	+5845	+15314

$$RT \log_e c = W = -3100 + 18.1T - 0.05T^2.$$

As in the example given above the formula with three constants represents the observations surprisingly well,

and within the limits of experimental errors. Just as in the previous case A_0 is negative, *i. e.*, the substance is absolutely insoluble at extremely low temperatures—which in reality are not accessible for experiments. B is positive, *i. e.*, the solubility increases to begin with, which is a necessary consequence of what has been said regarding the insolubility at 0° abs., and C is negative, *i. e.*, the numerical value of the heat of solution (if negative as in normal cases) decreases with rising temperature (or increases if positive as for $Ca(OH)_2$). As A_0 and C always have the same sign U is zero at a certain temperature; in the two examples given above this point lies at 548° abs. (= 275° C.) for boric acid and at 249° abs. (= − 24° C.) for $Ca(OH)_2$. The point at which A has its maximum value and is equal to U lies for boric acid at 680° abs. (= 407° C.) and for calcium hydrate at 220° abs. (= − 53° C.). These temperatures are inaccessible experimentally as well for the calcium hydrate as for the boric acid.

The calcium hydrate in saturated solution is dissociated electrolytically to a degree of 81 per cent. Therefore its osmotic pressure is 2.62 times greater than if the molecules were simple. In order to correct for this peculiarity van't Hoff introduced the coefficient i, so that the constant R has 2.62 times greater value than for gases and undissociated substances. Hence also the A and U should be multiplied by this factor. If this is done we find at 18° C., the heat of solution (U) equal to 2,930, whereas Thomsen found experimentally 2,800, a very good agreement. For boric acid Berthelot found $-U = 5{,}600$, whereas the calculation above gives −5,400, which is also in good agreement within the experimental errors.

I have found only a single class of dissolved substances, for which the rule that A_0 and C are negative and B positive does not hold. This class is fluids, which are only partially immiscible with water. As these substances are also highly interesting from other points of view, I have calculated three typical examples, namely ethyl ether, 2-4-6 trimethyl pyridine and phenol. For ether the solubility in the investigated interval decreases with rising temperature, for phenol it increases steadily and for trimethylpyridine it at first decreases and thereafter increases. The solubility c is given in gram-molecules per kilogram.

ETHYL ETHER, $C_2H_5OC_2H_5 = 74$ (KLOBBIE).

t	T	c	$\log_{10} c$	W obs.	W calc.	Diff.	dW/dt	U
− 3.5	269.5	1.63	0.2123	262	260	+ 2	—	+4812
+20	293	0.857	0.9329–1	− 90	− 90	0	−15.0	+3756
40	313	0.597	0.7762–1	−320	−321	+ 1	−11.5	+2787
60	333	0.48	0.6810–1	−485	−483	− 2	− 8.3	+1753
80	353	0.368	0.5667–1	−699	−587	−112	−10.7?	+ 653

$$W = RT \log_e c = 10{,}623 - 60T + 0.08T^2.$$

2-4-6 TRIMETHYL PYRIDINE, $(CH_3)_3\ C_5H_2N = 121$ (ROTHMUND). Crit. Point 5.7°.

t	T	c	$\log_{10} c$	W obs.	W calc.	Diff.	dW/dt	U
10	283	0.6404	0.8065–1	− 250	− 607	+357	—	+3746
20	293	0.2819	0.4500–1	− 737	− 753	+ 16	−48.6	+3342
40	313	0.1593	0.2021–1	−1141	−1104	−137	−20.2	+2495
80	353	0.1428	0.1547–1	−1364	−1349	− 25	− 5.6	+ 628
120	393	0.1537	0.1866–1	−1461	−1450	− 11	− 2.5	−1461
160	433	0.2417	0.3832–1	−1221	−1339	+118	+ 6.0	−3772
180	453	0.3024	0.4806–1	−1075	−1098	+ 23	+ 7.3	−5013

$$W = RT \log_e c = 9{,}352 - 55T + 0.07T^2.$$

PHENOL, $C_6H_5OH = 74$ (ROTHMUND). Crit. Point 68.8°.

t	T	c	$\log_{10} c$	W obs.	W calc.	Diff.	dW/dt	U
0	273	0.761	0.8816–1	−148.3	+174	−322.3	—	+ 5508
20	293	0.898	0.9534–1	− 62.1	− 71	− 11.1	+ 4.3	+ 983
40	313	1.044	0.0188	+ 26.9	+ 16	+ 10.9	+ 4.5	− 3859
50	323	1.296	0.1125	+171.2	+190	− 18.8	+14.4	− 6408
60	333	1.828	0.2644	+426.5	+424	+ 2.5	+25.5	− 9022
65	338	2.402	0.3805	+622.4	+584	+ 48.4	+39.2	−10572

$$W = RT \log_e c = 35{,}328 - 238T + 0.4T^2.$$

The points for which U is zero are 364° absolute (91° C.) for ether, 365.5 (92.5° C.) for trimethylpyridine, which also results from the minimum of c at that point, and 299.1 (= 26.5° C.) for phenol. This last point does not agree with the observations, for nothing indicates a minimum of c at that point, but as we see, we cannot speak of an agreement between the calculation and observation below 20° C. The same is true for the temperature above 60° for ether (perhaps this is partly due to errors of observation) and below 20° C. for the trimethylpyridine. The point, where $A = W + 2T$ has its minimum value and $A = U$ falls at 362° (= 89° C.), 379° (106° C.) and 295 (= 22° C.) for the three substances. This point is clearly visible for trimethylpyridine and for phenol. For ether this point lies above the temperatures examined. U is for ether 4,500 cal. at common temperature according to an observation by Le Chatelier. The agreement is satisfactory. It is evident that the ground for the abnormal behavior of these substances lies in the very great positive value of C, *i. e.*, d^2A/dt^2 in the examined interval of temperature. As is seen from the figures of dA/dt, d^2A/dt^2 is by no means constant in this interval, and it is therefore not to be expected that a constant value of C will allow an extrapolation. This is exceedingly clear for phenol, and the observations regarding the other two substances leave no doubt that an extrapolation with a constant value of C cannot give reliable results. These observations fall in the neighborhood of the critical points of these mixtures and it is well known that the simplified formulæ of van't Hoff, in which the volume of the fluid is omitted are not applicable in the neighborhood

of the critical point. We shall later see this assertion exemplified. Hence we ought not to draw conclusions regarding the values of A_o, B and C for these substances from the formulæ given above, which are only interpolation formulæ. The great value of C causes an abnormally high negative value of B and this in its order gives rise to the wholly abnormal positive value of A_o. But still one regularity remains, namely that A_o and C are of the same sign and opposite to that of B. In other words U passes through zero at some point and the U- and A-curves intersect at some point (above absolute zero). But we should not draw any conclusions regarding the real values of A_o, B and C from these experiments.

Van't Hoff has determined a great number of heats of solution from observations regarding solubility and compared them with observed data. This list of substances is the following (U expressed in great calories):

Substance.	Solubility in Per Cent.		Heat of Solution ($-U$). Observed.	Calculated.
Succinic acid.....	2.88 at 0°,	4.22 at 8.5°	6.7	6.9
Salicylic acid.....	0.16 at 12.5,	2.44 at 81	8.5	8.0
Benzoic acid	0.182 at 4.5,	2.19 at 75	6.5	6.8
Amyl alcohol.....	4.23 at 0,	2.99 at 18	−2.8	−3.0
Anilin.....	3.11 at 16,	3.58 at 55	0.1	0.7
Phenol.....	7.12 at 1,	10.2 at 45	2.1	1.4
Mannite.....15.8	at 17.5,	18.5 at 23	4.6	4.9
Mercuric chloride.	6.57 at 10,	11.84 at 50	3.0	2.7
Boric acid.....	1.95 at 0,	2.92 at 12	5.6	5.2

Van't Hoff also introduced for these substances, which are nearly perfect non-conductors, a magnitude i, similar to that spoken of above for calcium hydrate. As this magnitude i depends upon the dissociation of the substances,

$$i = 1 + (n - 1)\alpha,$$

where n is the number of ions, into which the electrolyte dissociates and α is the degree of dissociation, and α in all these cases is practically equal to zero, I have recalculated the figures, putting $i = 1$. In reality they have not changed much.

Van't Hoff has also given figures for some electrolytes which are dissociated to such a degree that we must take i as greater than unity, as for $Ca(OH)_2$ above. The influence of the dissociation is easily understood in the case of gases. If the gas does consist of just the simple molecules, indicated by its chemical formula, we may substitute $RT.c$ for p where c is the concentration. But if every one of the molecules, represented by the formula, is split up into i molecules (ions) then the pressure is i times greater than that calculated from the formula $p = RTc$. It is easy to see from the deduction of the formula above, that the same is valid also for solutions, namely that we must multiply c by i, in order to get correct values. That is what we have done above for calcium hydrate, in which case i may be taken as a constant. But in other cases, especially where the solubility increases with temperature, as in normal instances this is not permissible but we ought to tabulate $A = iRT\ (1 + \log_e ic)$.

Van't Hoff supposed that i is constant and found a good agreement between the observed and the calculated figures. Probably a revision of the figures will also verify the ideas of van't Hoff; at present it may suffice to indicate, how the recalculation has to be performed. I reproduce only some few figures calculated by Noyes, regarding silver salts, showing an excellent agreement with the figures observed by Goldschmidt.

Salt.	$AgC_2H_3O_2$	$AgC_3H_5O_2$	$AgC_4H_7O_2$
Heat of solution obs.	4,613	3,980	2,860
Heat of solution calc.	4,562	3,928	2,836

I now come to the most interesting case regarding the energy of solutions, namely the change of free energy on electrolytic dissociation and the simultaneous evolution of heat. We shall see that the circumstances are very similar to those observed in the solution of substances.

We begin with examining some substances which have been accurately investigated in a rather great interval of temperature, and thereafter consider other substances, which have not been measured so thoroughly.

In his great Carnegie-Institute memoir, which I have so often cited, Noyes gives some figures for the dissociation constants of water, acetic acid, ammonia and phosphoric acid, at different temperatures in a rather great interval, so that they may well serve as instructive examples of the variation of affinity of electrolytes.

The interpolation formulæ used for representing the A-values are for

Water; $\overset{+}{H} + \overset{-}{OH} = H_2O$; $A = 21420 + 29.91T - 0.085T^2$.

Acetic acid; $\overset{+}{H} + \overset{-}{CH_3CO_2} = CH_3CO_2H$; $A = -5360 + 14.66T - 0.0615T^2$.

Ammonia; $\overset{+}{NH_4} + \overset{-}{OH} = a NH_4OH + (1 - a)(NH_3 + H_2O)$; $A = -8625 + 32.63T - 0.0851T^2$.

Phosphoric acid; $\overset{+}{H} + \overset{-}{H_2PO_4} = H_3PO_4$; $A = -1955 + 11.9T - 0.0446T^2$.

It is interesting to see how well these interpolation formulæ represent the observations. I therefore give

below the observed and the calculated values of A. The next column contains the difference $A_{obs.} - A_{calc.}$ After this the value of dA/dt calculated from $A_{obs.}$ is tabulated. I gives the temperature in °C., T is the absolute temperature.

WATER.

t	T	A obs.	A calc.	Diff.	$-dA/dt$
0	273	−18780	−18795	+ 15	——
18	291	−19070	−19064	− 6	16.1
25	298	−19190	−19181	− 9	17.1
100	373	−21000	−21010	+ 10	24.1
156	429	−22850	−22987	+137	33.04
218	491	−25440	−25783	+343	41.77
306	579	−31160	−30801	−359	65.00

ACETIC ACID.

t	T	A obs.	A calc.	Diff.	$-dA/dt$
18	291	− 6306	− 6300	− 6	——
100	373	− 8446	− 8446	0	26.1
156	429	−10330	−10391	+ 61	33.7
218	491	−12940	−12990	+ 50	42.0
306	579	−18150	−17486	−664	59.2

AMMONIA.

t	T	A obs.	A calc.	Diff.	$-dA/dt$
0	273	− 6058	− 6056	− 2	——
18	291	− 6337	− 6331	− 6	15.5
25	298	− 6463	− 6456	− 7	18.6
50	323	− 7002	− 6962	− 40	21.6
75	348	− 7612	− 7573	− 39	24.4
100	373	− 8302	− 8284	− 18	27.6
128	401	− 9066	− 9217	+151	27.3
156	429	−10202	−10283	+ 81	41.3
218	491	−12894	−13113	+219	43.4
306	579	−18610	−18147	−463	64.9

PHOSPHORIC ACID.

t	T	A obs.	A calc.	Diff.	$-dA/dt$
18	291	− 2638	2629	− 9	——
25	298	− 2761	2749	−12	17.6
50	323	− 3181	3178	− 3	16.8
75	348	− 3689	3665	−24	20.3
100	373	− 4208	4203	− 5	20.8
128	401	− 4860	4876	+16	23.3
156	429	− 5585	5623	+38	25.9

The temperature interval is not so very great for the observations on H_3PO_4; therefore this example is of much less value than the other series. At high temperatures the differences between the observed and calculated values increase, which may perhaps be due to the difficulty of these observations, perhaps also to the circumstance that the higher members in the interpolation formula have been omitted and probably to both of these circumstances. The great negative values of these differences at $T = 306$, compared with the positive values at the nearest temperatures $T = 156$ and $T = 218$, indicate that the coefficient D of the omitted term DT^3 is negative, *i. e.*, of the same sign as C. From this it also follows that the numerical value of C given above is a little too high.

All the four interpolation formulæ are of the same type, the values of A_o and of C are all negative, the B values are positive. Very remarkable is the circumstance that whereas the four values of A_o are rather different (in the proportion 11 to 1), the values of B do not change so much (only in the proportion 2.8 to 1) and still less is the variability of C (only as 1.9 to 1).

The characteristic point, where A has its maximum value, and where the A- and U-curves intersect, lies at the following absolute temperatures (at double this temperature A has the same value as at $T = 0$):

for H_2O; $T = 176$ ($t = -97°$ C.)
for CH_3CO_2H; $T = 119$ ($t = -154°$ C.)
for NH_3; $T = 192$ ($t = -81°$ C.)
for H_3PO_4; $T = 134$ ($t = -139°$ C.)

i. e., about 150 to 80 degrees below the freezing point of water.

The other characteristic point, where $U = 0$, and consequently the dissociation is at its maximum, lies:

for H_2O at $T = 502$ ($t = 229$)
for CH_3CO_2H at $T = 295$ ($t = 22$)
for NH_3 at $T = 318$ ($t = 45$)
for H_3PO_4 at $T = 209$ ($t = -64$)

It is easy to calculate the heat of dissociation from the variation of K with temperature. In drawing a curve through the points representing U as a function of temperature it is easy to find the temperature, where $U = 0$. This point will of course agree with that calculated above and I actually find from the curves the values $T_u = 502$ for water $T_u = 295$ for acetic acid and $T_u = 318$ for ammonia. The zero point of U for H_3PO_4 lies 64 degrees below zero of the thermometric scale and is therefore not accessible experimentally.

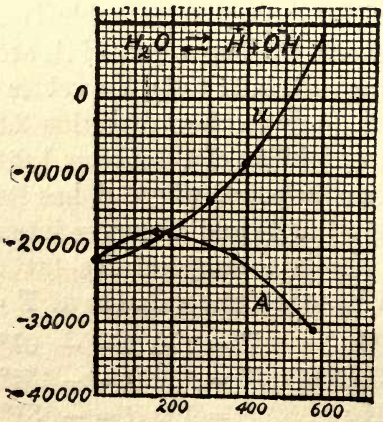

FIG. 5.

The great value of these observations depends upon their proximity to the zero of absolute temperature.

The interval of observed temperatures is about as great as that below 0° C. It is therefore probable that the formulæ will give nearly right results also below 0° C. and down to the neighborhood of absolute zero. I have given a graphic representment of the formulæ for water in the accompanying curves and in these I have also introduced the values of U calculated directly from Noyes' figures. If the U-curve had not a horizontal tangent at $T = 0$, the value of dA/dt would have an infinite value at the same temperature. In other words, the A curve ought there to run vertically and make an extremely sharp bend. This is not probable although not quite impossible.

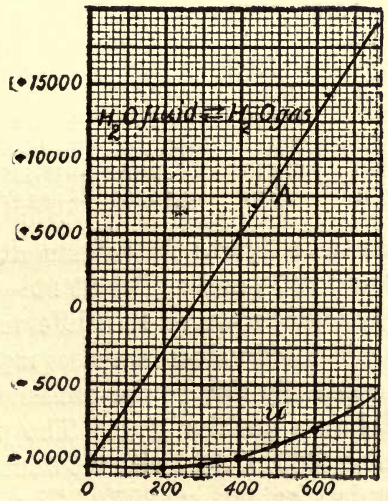

FIG. 6.

There are very few cases in which the A values are so accurately determined so near to the absolute zero and within so great an interval as just these. Only the A

values for transformation of vapor into water may compare with them, and to which I therefore wish to refer for a comparison. Here $A = RT\ (1 + \log_e p)$. Of course the value of A depends on the units in which p is expressed, for instance, millimeters of mercury or atmospheres. If, as generally done, p is given in millimeters, which unit I also use below, then A expresses the maximal work obtained in transforming steam at 1 millimeter pressure to water in a reversible way and at constant temperature.

FLUID WATER → WATER VAPOR.

$W = RT \log_e p = -11394 + 46.74T - 0.00927T^2$.

t	T	p obs.	p calc.	W obs.	W calc.	Diff.	dW/dt
−20	253	0.96	1.00	− 25	− 12	− 13	—
0	273	4.579	4.58	+ 825	+ 825	− 0	42.5
50	323	92.17	90.6	+ 2,901	+ 2,887	+ 14	41.5
100	373	760	760.3	+ 4,911	+ 4,909	+ 2	40.2
150	423	3,581	3,581	+ 6,870	+ 6,869	+ 1	39.2
200	473	11,625	11,639	+ 8,788	+ 8,789	− 1	38.4
250	523	29,843	29,101	+10,695	+10,665	+ 30	38.1
300	573	67,620	59,020	+12,650	+12,495	+155	39.1
350	623	126,924	90,440	+14,550	+14,127	+323	37.9

As is seen from these figures the agreement is excellent at 0, 100, 150 and 200°, and sufficient at − 20, 50 and 250°. At higher temperatures the difference between observed and calculated values increases rapidly. This peculiarity is evidently due to the omission of a term DT^3, where D has a positive sign. The proximity of the critical point (365° C.) is without doubt the cause of these irregularities (cf. p. 207). The attempt to give the formula without D a so great interval of validity as possible has brought about that the effect of D has partially been attributed to C which therefore is a little greater than in reality. To compensate for

this at low temperatures, B, which is of opposite sign to C, has also been taken a little too small and that has again caused a value of A_0, which is a little greater than in reality. Yet the error in A_0 is probably not greater than about 180 calories, *i. e.*, without appreciable importance. Differences of this order of magnitude may also be possible in the values of A_0 for the dissociation of electrolytes, but the errors in B/C and A_0/C are probably still less, so that an appreciable deformation of the curves is excluded.

It is noteworthy that if we designate p in another unit, *e. g.*, 1,000 mm. Hg, then $RT \log_e p$ decreases with $RT \log_e M/m$ where M/m is the ratio of the new and the old unit, *i. e.*, here 1,000. The decrease of A would then in this case be $1.985.T.2.3026 \log_e M/m = 13.71T$. In order to abolish the term $48.74T$ in the expression for A it would therefore suffice to designate the pressure in a unit which is 1000^m, where $m = 48.74 : 13.71 = 3.555$, *i. e.*, $4.62.10^{10}$ times greater than 1 mm. Hg. Of course this unit is of no practical value, at least at present.

A similar remark may be made regarding the dissociation constant of the electrolytes. If I use a unit, which perhaps is more consistent with the absolute system C.G.S. than the gram-molecule per liter, namely, the gram-molecule per cubic centimeter, all the values of K diminish in the proportion 1,000 to 1. Therefore A decreases by $13.71T.$, *i. e.*, the coefficient B decreases in its absolute value by 13.71. The magnitude of the coefficient B is here not so great as for the evaporation of water, therefore it is not necessary to change the units so much to get rid of the term BT. As units of volume should be taken instead of liter

for ammonia	0.0725	cubic millimeter.
for acetic acid	0.617	cubic millimeter.
for phosporic acid	2.5	cubic millimeter.

Instead of increasing the unit of volume in the said proportion we may diminish the unit of mass in the same proportion with the same result.

It is very easy to construct the curves thus transformed. It is only necessary to draw the tangent of the A-curve at the point $T = 0$ and to count the A-values from an axis going through the origin parallel to this tangent. Then the formulæ for A and U are

$$A = A_0 + CT^2 + DT^3 + ET^4 + \ldots,$$
$$U = A_0 - CT^2 - 2DT^3 - 3ET^4 \ldots.$$

At low values of T we may omit the higher terms including T^3 and T^4 and then the condition, demanded by Nernst for condensed systems, namely, that the A- and U-curves shall be related to each other as object and image in a mirror is true. But as soon as the higher terms T^3, etc., can no longer be neglected, which happens in the cases investigated above, at temperatures above 150 to 250 degrees, then the similarity of the two curves is spoiled.

There is no better proof of the small physical importance of the coefficient B than that it may be reduced to zero or given any value by changing the units of measurement. Therefore it is clear that an assertion that B is zero at the absolute zero would have very little meaning in this case. The case is somewhat different if in the homogeneous equilibrium between gases or dissolved substances the number of molecules does not change through the transformation or if we work with pure substances as in studying the dissociation of water or,

better said, with substances the concentration of which cannot be changed at constant temperature. But even in this case as we have seen above with water, there is no probability that the A-curve runs horizontally at $T = 0$, although special cases may agree rather well with this condition. This seems, for instance, to occur with some condensed systems, for instance with the transformation of rhombic sulphur into monoclinic as studied by Broensted. A_0 and C are not dependent on the adopted unit of pressure or concentration; the same is evidently the case with U.

The formula for the free energy A on transforming water vapor at 1 millimeter pressure into fluid water has the same form as the formulæ for the free energy on transforming ions of normal concentration into undissociated substances of the same concentration. But the constants are very different, so that the temperature where A has its maximum value occurs at first at 2,520° absolute, where of course these simplified calculations have no real meaning. Even the temperature where U vanishes is very high, it is calculated to 836° C. The said temperature occurs much sooner because of the positive value of D. As a matter of fact U is zero at the critical point 638° abs. On evaporation A goes through zero just at the point where the vapor pressure is equal to the arbitrarily chosen unit (here it is 1 millimeter and this pressure is valid at about −20°C.; if we had chosen 1 atmosphere A would have passed through zero at exactly 100° C.). An inspection of the curves giving A and U as functions of T shows that in the case of evaporation the part of the curves between 0° and 600° abs. corresponds only to the part of the A-

and U- curves for electrolytic dissociation, which lie between about 0° and 40° abs.

By differentiation we find:

$$\frac{dA}{dt} : \frac{dU}{dt} = \frac{B + 2CT}{-2CT} = -\left(1 + \frac{B}{2CT}\right).$$

If we know dA/dt and dU/dt at a given temperature (not too high), we may easily calculate $-B : 2C$, which is the temperature where A has its maximum (or minimum) value and the U- and A-curves intersect. In his inaugural dissertation Lundén has calculated all available values of dA/dt and dU/dt at 25° C. = 298° abs. With the aid of his table we calculate the following values T_m of the absolute temperature of $A_{max.}$ 298° absolute does not lie very high, so that probably the errors in the value of this temperature T_m are not so very great, perhaps some 30° C. Lundén also gives the values of A and U at 25°; it is rather interesting to see how far they have diverged from each other from the point of equality T_m. With Lundén, I have divided the material into three groups. The first contains bases, the second acids, which dissociate with absorption of heat, and the third those with production of heat at 25° C. Through the subtraction of the heat of dissociation of a weak acid from that of water we obtain the heat of neutralization of this acid with a strong base. In an analogous manner the heat of neutralization of a weak base with a strong acid is obtained and also the change of free energy on neutralizing the said substances. In the neutralization of weak acids with weak bases it is necessary to take the A and U values for both substances into consideration. In Lundén's work these

neutralization data are tabulated. I do not find it necessary to reproduce them.

FREE ENERGY AND HEAT IN IONIZATION PROCESSES AT 25° C.

	A	U	dA/dt	dU/dt
Water	−21,450	−13,450	−27	+ 50
Bases:				
Orthoaminobenzoic acid	−16,220	−10,220	−21	+ 52
Pyridine	−11,840	− 7,780	−13.5	+ 35.5
2, 4, 6 Trimethyl pyridine	− 9,110	− 5,510	−12	+ 77
Ammonia	− 6,440	− 1,160	−17.5	+ 58
Acids with negative heat of diss.:				
Boric acid	−12,570	− 2,960	−32	+ 12
p-Nitrophenol	− 9,750	− 4,840	−16.5	+ 21
Orthoaminobenzoic acid	− 6,780	− 3,270	−12	+ 38
Aminotetrazol	− 8,420	− 4,600	−13	+ 55
Cinnamic acid	− 6,070	− 400	−19	+ 31
Benzoic acid	− 5,690	− 200	−18.5	+ 42
Nitrourea (at 20°)	− 5,600	− 3,700	− 6	+100
m-oxybenzoic acid	− 5,560	− 100	−18.5	+ 26
m-nitrobenzoic acid	− 4,720	− 400	−14.5	+ 38
Nitro-urethane	− 4,470	− 2,900	− 5	+ 65
Salicylic acid	− 4,060	− 800	−11	+ 44
Acids with positive heat of diss.:				
Acetic acid	− 6,450	+ 110	−22	+ 31.5
Ortho toluylic acid	− 5,320	+ 1,310	−22	+ 30
Ortho chlorbenzoic acid	− 3,920	+ 2,240	−20.5	+ 35
Ortho iodbenzoic acid	− 3,900	+ 2,660	−22	+ 23
Ortho nitrobenzoic acid	− 3,000	+ 3,180	−20.5	+ 29
Ortho bromcinnamic acid	− 2,510	+ 3,280	−19.5	+ 28

	$-\frac{B}{2C.\ 298}$	T_m	A_0	B	C
Water	0.46	137	−21,420	+29.9	−0.085
Bases:					
Orthoaminobenzoic acid	0.60	179	−17,770	+23.2	−0.084
Pyridine	0.62	185	−13,070	+31.2	−0.087
2, 4, 6 Trimethyl pyridine	0.84	250	−11,980	+48.2	−0.060
Ammonia	0.70	209	− 8,625	+32.6	−0.085
Acids with negative heat of diss.:					
Boric acid	−1.67	(−497)	− 4,750	−20.2	−0.02
p-Nitrophenol	0.21	63	− 7,970	+ 4.5	−0.035
Ortho aminobenzoic acid	0.68	203	− 8,930	+26.2	−0.064

	$-\frac{B}{C2.298}$	T_m	A	B	C
Aminotetrazol	0.76	226	−12,800	+42.2	−0.092
Cinnamic acid	0.39	116	− 5,020	+12.0	−0.052
Benzoic acid	0.56	167	− 6,460	+23.2	−0.070
Nitrourea (at 20°)	0.94	277	−18,350	+93.5	−0.167
m-oxybenzoic acid	0.30	89	− 3,980	+ 7.7	−0.044
m-nitrobenzoic acid	0.62	185	− 6,060	+23.4	−0.064
Nitro-urethane	0.92	274	− 1,258	+59.7	−0.109
Salicylic acid	0.75	223	− 7,360	+33.1	−0.074
Acids with positive heat of diss.:					
Acetic acid	0.30	89	− 5,360	+14.6	−0.062
Ortho toluylic acid	0.27	80	− 3,160	+ 7.8	−0.050
Ortho chlorbenzoic acid	0.41	122	− 2,980	+14.4	−0.059
Ortho iodbenzoic acid	0.05	15	− 770	+ 1.0	−0.039
Ortho nitrobenzoic acid	0.30	89	− 340	+ 5.6	−0.049
Ortho bromcinnamic acid	0.30	89	− 890	+ 8.6	−0.047

These figures give a hint to many rather interesting conclusions, which will be more obvious if we smooth away the extremes by taking average values. These are for the three groups:

	n	A	U	A-U	dA/dt	dU/dt
Water	1	−21,450	−13,450	−8,000	−27	+50
Bases:	4	−10.925	− 6,168	−4,157	−16	+55
Acids with neg. U:	10	− 6,112	− 2,121	−3,991	−13.4	+46
Acids with pos. U:	6	− 4,183	+ 2,130	−6,313	−21	+29.4

	$-\frac{B}{2C.298}$	T_m	A_0	B	C
Water	0.46	137	−21,420	+29.9	−0.085
Bases:	0.69	206	−12,861	+33.8	−0.080
Acids with neg. U:	0.61	182.3	− 7,819	+32.3	−0.077
Acids with pos. U:	0.27	81	− 2,250	+ 8.7	−0.051

I have excluded the boric acid, which behaves quite differently from other acids, in taking the mean values. All the bases possess a negative value of U; they may therefore be compared with the corresponding acids. Although the heat of dissociation is about three times as great for the bases as for the corresponding acids,

the value A-U is of nearly the same magnitude for the two groups. The values $dA : dt$ and $dU : dt$ are also not very far from each other in the two groups; therefore the same holds true for the two values of $B/2C.298$ and T_m (the difference here reaches 12 per cent.). For the acids with negative U (at 25°) the value $A - U$ is 55 per cent. greater than in the foregoing two groups, dA/dt is about 1.5 times greater and $dU : dt$ on the other hand only 0.6 of the mean value of the two foregoing groups. A consequence of these last two circumstances is that T_m lies about 113° lower for the last group than for the two first ones. At this temperature A and U coincide and diverge at higher temperatures, therefore it seems quite natural that A-U shall be less for the two first groups, where the distance from T_m to the temperature of measurement is only 104 degrees, than for the third group for which the corresponding distance is 217 degrees. Evidently this circumstance as well as the low value of A_o is connected with the positive sign of U at 25° C. for this last group. At higher temperatures other acids will come over to the third group, thus for example m-oxybenzoic acid already at 29° and benzoic acid at 30°. The numerical values of A_0, B and C decrease continuously from the first to the third group, A_o in the greatest proportion, C in the least.

The most pronounced regularity is that $dA : dt$ is negative and $dU : dt$ positive for all substances examined, and that for all (except boric acid, which is very difficult to determine accurately because of its extreme weakness) the numerical value of $dU : dt$ exceeds that of $dA : dt$. A consequence of these regularities is that

T_m for all examined electrolytes has a positive value below 298° (the temperature of observation = 25° C.). The two highest values for nitro-urea and nitro-urethane fall at + 4° and + 1° C., after these comes trimethylpyridine with − 23° C., then there is a long distance of 24 and 27° C. respectively to the next two, aminotetrazol and benzoic acid. It must therefore be regarded as characteristic for the weak acids and bases, including water, that they possess A- and U-curves which intersect two times, not only at $T = 0$, but also at a higher temperature, and that they diverge from that temperature, so that $dA : dt$ is negative, $dU : dt$ positive and numerically greater than $dA : dt$.

Water has its place just in the middle of the two groups. A great part of the figures given above are deduced from determinations made by Lundén, the acids from aminotetrazol except acetic acid are determined by other authors. If we now compare the values of T_m according to the measurements of Noyes and those of Lundén, we find a certain difference; for water 176–137, for acetic acid 119–89, for NH_3 192–209. These differences are of course due to experimental errors, I am inclined to lay a great value on Lundén's determinations of ammonia, but for the other substances the determinations of Noyes seem preferable. The phosphoric acid belongs to the second group of acids, its dissociation into ions is accompanied by an evolution of about 1,600 cal. at 25°. Its T_m lies higher (at 134°) than that of those acids in general (81°). I suppose according to Noyes' measurements that the values of T_m deduced from the figures given by Lundén are a little too low, but on the whole this difference is of minor importance.

We have seen before that:

$$A = RT \log_e K \quad \text{and} \quad U = -RT^2 \frac{d \log_e K}{dT}; \; U_0 = A_0.$$

These equations are sufficient for the determination of A at any temperature if we know U at all temperatures. For then we know A_0 and $d \log_e K : dt$, *i. e.*, the variation of A with temperature. The old problem of the thermochemists, to determine the affinity, is therefore theoretically solved by means of these equations, given by van't Hoff.

But practically, there are rather great difficulties, which depend upon our lack of knowledge of the values of U, the heats accompanying chemical processes at all temperatures and especially very low or very high ones. A certain theoretical interest is attached to the vicinity of absolute zero. Of course aqueous solutions do not exist in the neighborhood of this temperature, so that the consequences of our equations cannot be verified there.

There A is negative and therefore $T \log_e K$ is negative and has a definite value; for $T = 0$ $\log_e K$ becomes negative and infinite, *i. e.*, $K = 0$. The dissociation disappears totally at absolute zero. Ions cannot exist at absolute zero, just as the vapors of liquids on similar grounds do not exist in the neighborhood of absolute zero.

It is of a certain interest to remark that the regularities are much more prominent with the process of evaporation than with that of solution or of ionization. In the first case we have the important rule of Dühring, and its modification by Ramsay and Young, as well

as its consequence, the rule of Trouton. It would be rather difficult to find something similar for the solubility or the dissociation of electrolytes. Regarding the free energy on evaporation I have found that the coefficient B is nearly a constant, about 44 for all substances. The curves representing A therefore run very nearly parallel to each other. As we have seen above for the three groups of electrolytes there is a certain parallelism between the magnitude of the constants A_0, B and C, so that they are greater for the bases and least for the acids with positive heat of dissociation. But it would give very absurd results if one supposed that this rule were applicable for the comparison of two electrolytes chosen at random. On evaporation the regularity is much more obvious although not complete.

On the other hand the multiplicity and variation of the phenomena is much greater in electrolytic dissociation and they therefore have a greater attraction for the student who wishes to learn all possible combinations appearing in the central problem of physical chemistry, namely that regarding chemical equilibria. This problem is classical here in the world-renowned Yale University, where one of the greatest thinkers in natural philosophy, the immortal Willard Gibbs, has devoted his genius to the investigation of chemical equilibria.

At the close of my lectures I feel deeply that I need to tell you how thankful I am for the great kindness you have always shown me and for the permanent interest with which you have taken part in my lectures. I hope that you will have found how considerably American

scientists have contributed to the most modern progress of physical chemistry. I am quite convinced that the development will go on still further in that direction, and I am glad to say that we expect very much from the excellent work of American colleagues with their open mind, their unrivalled experimental skill and their practical sense.

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APR 29 1967

APR 30 '67 -2 PM
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